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THE UNIVERSITY OF ALBERTA

DISCRIMINATION OF FLAT GLASS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS METHODS

by

STEVEN J. PITTS (C)

A Thesis

Submitted To The Faculty Of Graduate Studies And Research

In Partial Fulfilment Of The Requirements For The Degree

Of Doctor Of Philosophy

The Department of Chemistry

Edmonton, Alberta

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To

my family,

For their encouragement, attitudes toward life and

most of all their unconditional love.

Abstract

The focal point of this research was to discriminate among flat glasses having similar refractive indices on the basis of elemental composition. Instrumental neutron activation analysis (INAA), cyclic and epithermal INAA studies were performed on 19 glass samples provided by an RCMP forensic laboratory. Flat glass panes produced by two major Canadian manufacturers were studied using INAA and cyclic INAA. Several advanced statistical methods were employed for analysis of the data.

Using INAA, 90% of all pairwise comparisons of the nineteen glass samples were found to be distinguishable based on sodium, aluminum or calcium values at the 1-mg increment level (1% experimentwise error rate). This value dropped to 73% when 100-μg subsamples were considered. Aluminum was found to be the best element for discriminating between the various glasses, followed by sodium and then calcium. The formulations employed by the two flat glass manufacturers were readily discernible while the panes produced by a given manufacturer were homogeneous with respect to Na, Al and Ca for subsamples as small as 100 micrograms.

During optimisation of the hafnium signal-to-noise ratio using cyclic INAA, it was discovered that an overall correction factor that was simpler and more convenient could be employed instead of the usual live time - dead time correction procedure. Some heterogeneity was noted in the hafnium content of the glasses found within two of the four refractive index groups. Thirty three percent of all pairwise comparisons between glasses possessing the same refractive index were distinguishable on the basis of their hafnium values at the 1-mg increment level (1% experimentwise error rate). This rose

to 52% at the 5-mg increment level, but no additional discrimination of the fifteen glasses was provided by hafnium at either increment level when comparison of the results with those for Na, Al and Ca was performed. No statistically discernible difference was found between the hafnium levels for the two manufacturers, and hafnium was homogeneously distributed in all the panes.

Finally, no new elements suitable for the discrimination of flat glass samples were discovered when a boron carbide shield was employed to reduce interference by sodium activation.

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I would like to thank my supervisor Byron Kratochvil for his kind assistance and general enthusiasm for this project. I would also like to thank all members of the research group for providing a very interesting and enjoyable working environment.

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I would like to acknowledge the use of the University of Alberta SLOWPOKE-2 reactor facilities during the course of this investigation. In addition, John Duke, Peter Ford, Gordon Haverland and Dennis Ng have all contributed suggestions, encouragement and friendship.

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In chapter 4 of this thesis, the fabrication of the B_4C shield was possible due to the experience of John Wilson and Richard Flanagan.

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Chapter 1

Introduction

1.1.1 Soda-Lime Glass Formulation

Fusion of silica (SiO_2, sand), soda/potassia (Na_2O/K_2O), calcia (CaO, lime), magnesia (MgO) and alumina (Al_2O_3) and the subsequent cooling of this melt to a kinetically stable rigid condition, without crystallisation, results in an amorphous material commonly referred to as soda-lime glass. These major components are deliberately added and carefully controlled by the manufacturer to produce specific glass properties. The structural backbone of soda-lime glass is comprised of SiO_4 tetrahedra (silicates) which have aggregated to form an extended three-dimensional network. Upon cooling, this network rapidly increases the viscosity of the molten glass and effectively prevents crystallisation (devitrification) by impeding the formation of nucleation sites[1]. Formation of alkali silicates, upon introduction of alkali oxides to the fundamental network, results in a significant decrease in the melting temperature. In addition, the random cleavage of some oxygen-silicon bonds, connecting SiO_4 tetrahedra, with the concomitant location of sodium and potassium cations around these negatively charged centres, produces a much more open structure. This decreases the viscosity of the melt and permits a more easily worked material. While the chemical resistance of a glass to atmospheric moisture and carbon dioxide is enhanced by the addition of calcia and alumina, the alkaline earth oxides provide fluidity. A typical soda-lime window glass composition, in weight percent,

would consist of the following : SiO_2 (72), Na_2O/K_2O (13), CaO (8), MgO (4) and Al_2O_3 (1). The above formulation refers to window glass of "modern" manufacture. This distinction has been made since the MgO content has been closely controlled since 1930. Prior to this period, much lower MgO levels were common.

In addition to these major components, several other elements comprising two classes may be noted. The first class involves elements found at trace levels which are introduced to the glass as impurities in the raw materials. Their concentrations, beyond having a strict maximum limit, are not controlled by the manufacturer but are uniquely dependent on the particular raw materials employed. The most ubiquitous contaminant of this nature is iron, as Fe_2O_3 or Fe_3O_4 , which can impart a colouration to glass when present at several hundredths of a percent[2]. Essentially, all the raw materials contain iron to a greater or lesser extent. Additional sources may include the dissolving of refractories employed as blocks in the glass furnaces, machinery used in manipulating the cullet, and the cullet itself as well as any equipment used in the handling of the finished product. Cullet refers to waste glass either from the production process or obtained by a manufacturer from external sources which is employed to supplement a batch. It is added as any other raw material and generally constitutes one quarter to one half the total charge[3]. Other unwanted colouring agents include Cr, Cu, Co, Ni, V, Mn and S. It should be noted, at this point, that all the major oxide constituents of glass may be present to a certain extent in each of the raw materials. For example, sand characteristically contains alumina, lime and magnesia which need not be considered impurities. Their presence must, however, be uniform in amount so batch formulations can be amended. Chloride, as NaCl

or KCl, may be present in soda ash (Na_2CO_3) or potash (K_2CO_3) as a by-product of their refining processes. Other sources of trace elements become apparent upon considering the glass manufacturing process. As mentioned previously, raw materials come in intimate contact with refractory materials serving as the lining for glass furnaces. Hence, the introduction of siliceous materials, alumina and zirconia (ZrO_2) results due to the corrosive nature of the melt. Fuels used to heat the glass may also contribute to the trace impurity levels.

Elements in the second class are added intentionally by the manufacturer to impart colour. Vanadium (yellowish-green), cobalt (violet-blue) and chromium (emerald green) as well as iron, manganese, uranium and others have been used as dissolved oxides. Gold, silver and copper are the best known examples of colour produced by colloidal particles. Physical decolourisation, on the other hand, employs the notion of adding elements that form complementary colours to mask any unwanted colouration in a glass. For example, since the green colour of iron is the result of preferential absorption at the ends of the visible spectrum rather than the middle, correction of this deficiency should be possible by absorption of wavelengths in the centre of the visible region. Modern practice employs the pink of selenium and the violet-blue of cobalt to counteract this green. More recently, ceric oxide has been used in conjunction with selenium and cobalt to reduce the cost of decolourisation. In contrast to physical decolourisation, chemical decolouration works on the principle of oxidising any iron present. Manganese dioxide is the classic example of a chemical decolouriser. Although historically significant, chemical decolourisation has yielded to physical decolourisation in modern flat glass manufacture because it is a

more reliable and more easily controlled process when glass furnaces are employed.

1.1.2 Modern Flat Glass Manufacture

Glass may be classified according to its mode of production or its end use. The major glass types include flat, container, tableware, vehicle headlight and other specialty glasses (e.g. lightbulb glass, eyeglass lenses and phosphosilicate glasses). Flat glass is a generic term which designates the type of glass commonly found in mirrors and in the windows of domestic, commercial and industrial buildings. Plate glass, used in doors and windows, is also included in the flat glass category. The discovery of thermal tempering and the chemical toughening of flat glass has even permitted its use in car and aircraft windshields. Although the domestic flat glass market in Canada is served by two major manufacturers, a significant volume of glass is imported[4].

Modern Canadian flat glass manufacture began at the turn of the century in Thorold[5], Ontario. Pilkington Brothers Limited (United Kingdom) eventually relocated in Scarborough, Ontario and were the original parent company of what is now AFG Glass Incorporated. Pittsburgh Plate Glass Canada Incorporated (Owen Sound, Ontario), whose parent is the American giant Pittsburgh Plate Glass Company, is the other major Canadian flat glass manufacturer.

Characteristically, the raw materials employed in modern glass manufacture are pure, reliable in composition, abundant and physically suitable. Ideally, contaminant free batch ingredients are desired but in practice

sufficiently low iron and impurity levels are adequate. An abundance of raw materials ensures flat glass production is economically viable while a reliable composition aids the finished product quality. To ensure product quality, suppliers of the raw materials must meet rigid product specifications fixed by the glass manufacturer. The raw materials comprising a batch may either be weighed out manually or automatically, the appropriate method being dictated by the size of the batch as well as the extent of the operation. An accuracy of two parts per thousand[6] for the major ingredients is easily attainable. Colourants and minor constituents are weighed separately on smaller balances and are premixed before addition to the bulk. Mixing consists of tumbling in a revolving drum equipped with blades for effective lifting and spreading of the solid material.

In the tank furnace the flames come directly in contact with the raw batch and molten material. Introduction of the mixed batch occurs at several places along the length of the tank. As a result, even spreading of the batch is desirable since the batch may act as an insulator in areas where the batch is quite thick while too thin a coverage may result in foam or silica scum forming on the bath surface. Both these occurrences prevent heat from penetrating into the melt with the fining and proper homogenisation of the glass being hindered. Fining of the melt refers to the escape of gas bubbles due to the viscosity decrease associated with the fusion process. Gases trapped between sand grains, soda ash and lime; produced from reactions within the melt and soluble in the melt itself must all be discharged. Sodium sulphate (saltcake-typically added at the 0.1 weight percent level) is commonly used in flat glass manufacture not only as a fining agent but also as an agent for dissolving any silica that has escaped solution. Removal of residual gas is also

significant from the standpoint that it produces a stirring action promoting homogeneity of the melt. Different furnaces have been designed, all of which restrict any unmelted batch or melt scum from reaching the working end. Homogeneity is promoted by diverting the melt and thus extending the length of time required to traverse the tank from melting to working end. Due to thermal gradients within the furnace and melt, homogeneity is also furthered by convection. The tanks are run continuously with raw materials being fed into the tank at a rate which just counteracts the withdrawal of molten glass. Common dimensions for the continuous tank furnaces are a depth of 5 feet, a width ranging from 30 to 35 feet and a length spanning 100 to 200 feet. Typically, 1500 molten tons of glass may be present in the furnace at any time. These dimensions reflect the fact that glass of high quality (free from bubbles and other defects) is needed. Temperatures between 1500 and 1600 °C are employed to melt the batch. The working temperatures of molten glass are somewhat cooler than those of melting. By flowing the molten glass toward the working end and away from the direct heat of the fires, cooling is promoted.

Both of the major Canadian flat glass producers use the float glass production process. The term flat glass formerly encompassed different production methods for sheets and plates. Sheets were produced by drawing the molten glass vertically, with subsequent cooling of both surfaces freely in air. Physical contact with rollers or other forming elements was avoided until the sheets were relatively hard. This resulted in a bright and transparent glass which possessed a "fire-polished" surface. However, stretching of the molten glass led to small differences in viscosity due to chemical and thermal inhomogeneities[7]. As a result of thickness variations in the glass ribbon,

undesired optical distortions arose. Plate glass, on the other hand, was produced by physical contact with forming elements, generally rollers, and any imperfections in these elements resulted in their faithful reproduction in the glass itself. As a result, mechanical grinding and polishing was necessary to produce a transparent pane of glass. Plate glass, unlike sheet glass, was free from optical distortion since its plane polished surfaces were of a high degree of parallelism. The float glass process, introduced in 1959 by Pilkington Brothers Limited, was intended to combine the desirable characteristics of both methods by supplying an optically true surface without the need for its physical alteration.

In the float glass process, the molten glass arrives at the working end of the furnace at a temperature of about 1050 °C and is then allowed to spread out over the clean surface of a molten tin bath. Throughout this stage in the manufacturing process, the glass is surrounded by a controlled atmosphere to prevent oxidation of the molten metal. Under the combined influence of gravity and surface tension, the surfaces of the glass are essentially optically true (approximately flat and parallel). As the ribbon of glass is pulled across the molten tin bath it is progressively cooled and upon reaching a temperature of 600 °C the ribbon is sufficiently viscous to permit lifting it from the bath by tractive force applied by a rolling conveyor. In this process, called forming, glass thicknesses between 2 and 25 mm can be produced. Modern production practices permit a single float bath to form up to 5500 tons per week of molten glass. After forming, the molten glass moves continually along the rolling conveyor into an annealing oven or lehr. Here, the glass passes through various sections, each under close thermal control. The annealing process is designed to prevent or relieve the internal strains

normally brought about in production. Since the interior of a glass sheet cools more slowly than the exterior, these strains arise from the creation of temperature gradients. Annealing reheats the glass and thereby reduces its viscosity. Molecular movement is then possible and acts to relieve the internal strains. By gradually cooling the glass to rigidity, the creation of internal strain is avoided to a large extent. The finished product is then machine cut into panes of any desired size.

Initially, the discrimination of flat glasses focused on physical properties. The physical characteristics (refractive index, density, dispersion, etc.) of a glass are, however, dependent not only on the composition of a glass but also are a function of the heat treatment which it received in the annealing oven[8]. Consequently, density, refractive index and dispersion measurements are not sufficient for discrimination within a particular glass type. In addition, modern production practice has led to less variation in the physical properties of flat glasses. For example, window glass in Britain (manufactured after 1945) has a refractive index in the range of 1.515 to 1.518[9] and a density of 2.43 to 2.52[10]. Therefore, chemical methods have been introduced in recent years to discriminate between flat glasses possessing widely variant chemical compositions.

1.2.1 The Discrimination of Flat Glass By Chemical Analysis

A large section of the chemical literature is concerned with the identification and analysis of glass submitted as evidence in criminal investigations. In some cases fragments of glass, found on clothing, are only 0.2 to 0.5 mm in maximum dimension. Fragments of this size correspond to a mass of approximately 100 micrograms[11]. Therefore, proposed chemical

methods should be able to allow routine analysis of samples in the milligram to submilligram range.

In 1976 Hughes and co-workers[12] reported an atomic absorption spectroscopy (AAS) method for the determination of manganese and magnesium in glass. The glass fragments analysed were approximately one milligram in size. Graphite furnace atomic absorption spectroscopy (GFAAS) was performed for manganese but magnesium was determined by conventional flame (air-acetylene) AAS. For routine analysis, an average percent relative standard deviation (RSD) of 10 was accepted for magnesium concentrations in excess of one percent. Similarly, for manganese concentrations above 30 parts per million (ppm), the RSD was 9% on average. Both of these values were based on twenty samples. In their study, magnesium levels in sheet glasses were found to have a high degree of correlation with the refractive index. The manganese concentrations were shown to exhibit little correlation. In addition, the differentiation between various sheet glasses using these two elements was found to be poor. Upon comparison, only 43% of the sheet glass pairs were distinguishable. A homogeneity study also involved the analysis of a sheet of window glass for magnesium and manganese. The results indicated that the variations which occurred in replicate analyses were attributable to experimental limitations and not to variations in the elemental distribution within the sample.

Howden et al.[13] studied iron and magnesium concentrations in small glass fragments using GFAAS. Sample preparation involved digestion of the samples with hydrofluoric acid followed by heating at 110 °C for one hour. Suppression of the iron absorbance signal in the presence of silica was observed. No matrix effects were observed for magnesium. The relative

standard deviations for iron and magnesium were 8 and 11% respectively. These were obtained for eight replicate analyses on approximately 100-µg fragments of a sheet glass.

Catterick and Wall[14] have reported a flame AAS method for the measurement of magnesium, manganese and iron in glass fragments ranging from 250 to 500 micrograms (µg). Sample dissolution involved cold acid (HF-HCl) digestion followed by simple dilution with distilled water. Nebulisation of discrete sample aliquots (200 microlitres) was performed and the resulting pulse absorption signal was recorded. Although magnesium and iron were determined for samples of approximately 100 µg, manganese could not be determined below 200 µg. The routine analysis of 500-µg samples resulted in 5 (Mg), 5-10 (Mn) and 10 (Fe) percent relative standard deviations for ten analyses. Results obtained on the same day, for 20 replicate analyses performed on 100-µg samples, resulted in percent relative standard deviations of 5.6 and 11.0 for magnesium and iron respectively. An interesting observation arising from this research was the enhancement of the manganese signal by magnesium when GFAAS was employed. Repetition of the same experiment using an air-acetylene flame resulted in no observable enhancement of the signal.

In trying to avoid the long analysis times and low sample throughputs associated with GFAAS, Headridge and Riddington[15] introduced single glass chips (ranging between 0.1 and 10 mg) directly into the furnace. An inductively heated graphite furnace was used to determine trace amounts of silver and lead in float and sheet glasses. Silver concentrations were found to be more variable than those of lead. The analysis of a float glass sample resulted in a 3 and 13.5% average RSD for the lead and silver contents

respectively. Two sheet glass samples were also analysed. An average RSD of 8% was found for lead in both samples but values of 12 and 30% were obtained for silver. This latter value was associated with a silver level of 0.007 μg/g sample. Six glass fragments were studied in each case.

While AAS has shown considerable promise, the inability of this technique to perform multielemental analyses has hindered its further implementation. Other problems associated with this method include the determination of those elements, such as Ca, which form insoluble fluorides. The formation of refractory carbides by Ba, for example, also posed a problem when a graphite furnace was employed.

Emission phenomena have been studied by a wide range of analytical techniques. Harvey[16] described a direct current arc emission spectrographic method that consumed as little as 25 to 50 μg of sample. The results were semiquantitative in nature, this limitation being due to procedural conditions such as timing exposures on the order of one second and problems with weighing samples as small as 25 micrograms. This latter restriction was imposed by a balance having only a 3–μg sensitivity. In 1976, a quantitative six element survey was reported[17]. Glass samples of approximately 1 mg were analysed with exposure times for a complete burn ranging from 1.50 to 1.75 minutes. The various elements were determined with precisions ranging from 4 to 13% RSD when 6 replicate samples were analysed on the same photographic plate. In a study of seven sheet glasses, the correlation between element concentration and refractive index decreased in the following order : Ca, Mg, Fe, Mn, Al and Ba. Based on these results, the authors expected Mn, Al and Ba to be the most useful elements for discriminating between samples with similar refractive indices. Further investigation showed that barium

levels alone were able to discern 11 of the 21 possible pairs formed from the seven sheet glass samples. Aluminum was the only other useful element, with discrimination between a further two pairs being possible. Calcium, which has a high degree of correlation with refractive index, was of no value in the discrimination of sheet glasses. Despite these investigations, the widespread use of direct current arc emission spectrography has generally been precluded by its dependence on an involved sample preparation stage and on the inordinate amount of time associated with the extraction of quantitative data from photographic plates.

Replacement of the arc source by a laser[18] made possible the analysis of very small glass samples by laser emission spectroscopy. The technique relied on the following sequence of events. A vapour plume was generated by impingement of a laser on the sample of interest. This plume increased the conduction between two graphite electrodes, causing them to discharge and, hence, excite the atoms in the vapour. Photoplate detection recorded these events. Experimentally, nine replicate analyses of a glass confirmed the presence of Ca, Si, Ba, Cu, Ti, Pb, Mg, Al, Fe, Mn and Sr in the sample. Precisions between 5 and 10% RSD were generally obtained with Al (2.8%) and Cu (30.7%) being the exceptions. Since the determination of elements below about 150 to 200 ppm was not possible, the authors expected discrimination among modern window glasses to be difficult. The minimum sample size for this technique was between 0.5 and 1.0 milligram.

German and Scaplehorn[19] considered spark source mass spectrometry (SSMS) for the rapid analysis of small glass fragments. Electrodes were constructed of graphite and powdered glass by compression in a suitable die. In early experiments less than 20% precision was not uncommon for a given

element. However, by ensuring that the location of the electrodes in the source and the spark gap distance were highly reproducible, results with a precision between 5 and 10 % relative standard deviation were generally obtained for 4 replicate measurements. The introduction of flat-ended electrodes also reduced any effect resulting from the change of electrode shape during sparking. Reduction of the sample size to less than 5 mg (the smallest sample considered for this study was 1.5 mg) necessitated the use of pointed electrodes. As a result, the precision decreased to 10-15% RSD for 6 replicate measurements. The elements determined in this study were Ti, Fe, Mn, Rb, Sr, Zr and Ba, with the addition of V, Co, As, Sn, Sb, La, Ce and Pb when at least 5-mg samples were analysed. Significantly, the trace element concentrations of these glasses were found to be characteristic of a particular manufacturer and a specific site of production. In a follow-up to this report[20], 20 window glass samples indistinguishable on the basis of physical properties were studied. Excluded from the previous study were As, Sn, Sb and Pb. From this set of 20 glasses, 2 glasses were chosen at random to serve as control samples (i.e. glass samples obtained at the scene of a crime). One analysis was performed on each glass in the set while 3 and 4 replicate measurements were performed on control samples one and two respectively. All of the glasses were distinguishable from the first control but only 16 of the 19 glasses were discernible from the second. These differences were reported for a 5% significance level.

Although Locke and co-workers[21] were concerned with the classification rather than the discrimination of flat glass samples, they reported a SSMS method for samples ranging between 100 µg and 1 mg. Six replicate determinations on 100-µg samples revealed percent relative standard

deviations between 30 and 50% for Mg, Fe, Mn, Rb and Ba, while the precision associated with the Sr determination was 71%. The poor precision associated with the radiofrequency spark source led to the introduction of other ion sources. Included among these were the hollow cathode[22] and the laser source[23,24]; neither has yet found wide application. Haney[25] considered isotope dilution spark source mass spectrometry (ID-SSMS) for the determination of absolute elemental concentrations in window glasses. Using this technique, a minimum sample size of 1 mg was necessary because of the reagent blank. Triplicate measurements on 10 mg samples revealed K, Rb, Sr, Zr and Ba were determined with a RSD of approximately 6 percent. Based on his experimental data, all of the above elements were found to be homogeneously distributed within two sampled window panes. Iron, lead and cerium levels were of little use for discrimination, however, because of their inhomogeneous nature. In one set of glasses 25 of 28 possible comparisons were found to be distinguishable at the 1% significance level, while 182 of the 190 possible comparisons were discernible in a second set. Despite these new directions, the long analysis times coupled with the complexity and expense of the instrumentation has hastened the decline of SSMS.

A scanning electron microscope/microprobe (SEM) equipped with a wavelength dispersive analyser was employed for the examination of glass by Vasan and co-workers[26]. Three different glass samples were distinguished on the basis of their sodium levels. By rastering the electron beam through a 100 X 100 μm area, the problem of migration of sodium ions, which leads to analytical bias, was prevented. Prevention of this migration, which occurs to a lesser extent for K, Ca and Ba[27], was also important from the standpoint that

the concentrations of the non-mobile elements in the phase would also be affected. Defocussing of the electron beam[28], coating the sample with a thin film of a conducting material[28], lowering of the operating voltage[29], cryogenic cooling of the sample[30], an empirical correction method[30] and even bombardment with neutral argon atoms[31] or a proton beam[32] are some of the alternative solutions suggested for resolution of this problem. Using energy dispersive X-ray spectrometry (SEM-EDX), Reeve et al.[33] found 2 of 81 glass samples to be indistinguishable. However, no indication of the sample size was given. Also, as Howden and co-workers[34] have pointed out, the density and refractive index data indicated that the bulk of these glasses could have been discriminated solely on the basis of physical properties alone.

Andrasko and Maehly[35] also swept an electron beam rapidly through a selected sample area of 80 X 80 μm. The following elements were found in the investigated glass samples : Ca, Na, Mg, Al, K, Ba, Si, S, Cl and Fe, but only the first six elements were suitable for the purpose of discrimination. Seven determinations on a single fragment resulted in a 1.3 to 3.6% relative standard deviation range for the Na/Mg, Na/Al, Mg/Al and Ca/K ratios. The Ca/Na values ranged from 6.6 to 10.1 percent. Slightly higher relative standard deviations were observed in the analysis of different samples from the same glass pane. Energy dispersive X-ray analysis, involving 7 locations on two window panes, showed no detectable variation in chemical composition over the sheet glass samples. Using SEM-EDX and analysing 3 fragments from each sample, 33 of 40 window glass specimens were distinguished. Additional analysis using emission spectrography resulted in 38 of the 40 window glass specimens being differentiated. It also appeared to the authors that the Ca/Na ratio of the samples increased with increasing

refractive index. Therefore, only rarely did this ratio discriminate between glasses with similar refractive indices. The chief limitation of a SEM equipped with an EDX spectrometer is that only concentrations greater than about 0.1 to 0.2% (i.e. only the major elements in glass) can be detected. The cost and complexity of the technique has also limited its use to a few larger facilities.

Howden and co-workers[34] reported two methods for the XRF analysis of glass fragments ranging between 100 micrograms and 2 milligrams. Samples were either presented as single fragments or as dispersions on filter paper. The precision values (RSD's) associated with peak area ratios for the analysis of four sheet glass fragments were typically 25% and 12% for 200-μg and 1-mg samples. Typical values for the dispersions were 11% (200 μg) and 5% (1 mg). Magnesium, calcium, silicon, potassium, titanium-barium (i.e. a peak due to coincident Ti-K_α and Ba-L_α lines), manganese and iron were quantitatively determined for 200-μg fragments and for dispersions of these same fragments. Fragment analysis resulted in no differences being found among 6 pairs of window glasses having refractive indices in the modern window glass range (1.517). On the other hand, three out of six pairs having refractive indices outside the modern window range (1.520) were discriminated. Using dispersed samples, 6 out of 12 window glass pairs were discriminated. The same workers[36] also tested 10 sheet glasses of refractive index 1.5160 and 10 float glasses of refractive index 1.5177 but poor discrimination was found once again. In a subsequent paper[37], fragments of glass as small as 40 μg were analysed reproducibly.

Lloyd[38] studied the fluorescence from glass surfaces on fragments as small as 0.05 mm^2 (18 μg). Several fluorescence features were identified, including a tin fluorescence typical of float glass surfaces. Across a pane of

glass, no statistically discernible difference was noted for the tin fluorescence (5% significance level). This, however, was not true of the bulk (i.e. the portion of glass not contacted by the molten tin) fluorescence. The tin fluorescence also had a negligible correlation with any refractive index feature. In a study involving 7 float glasses (refractive index range of 1.51716 to 1.51726, 0.3 cm^2 sample area) monitoring of the tin fluorescence allowed 20 of the 21 pairwise comparisons to be separated at the 5% significance level. An appreciable variation in relative fluorescence intensity also allowed float and nonfloat window glasses to be distinguished.

Phosphorescence[39], attributable to trace impurities in glass, has also been used as an investigative technique. This low-temperature (77K) luminescent property of glass permitted the discrimination of glass samples with identical refractive indices. Excitation with 270 and 425 nm radiation and monitoring of the ratio of the emission intensities at 740 and 550 nm (I_{740}/I_{550}) resulted in 17 of 21 samples being discriminated. When four other excitation wavelengths were used, the remaining samples were shown to exist as two dissimilar pairs. The practical lower limit for sample size appeared to be 1 mg, but smaller sizes were considered possible if the exciting radiation could be focussed to a small spot. For two windows, the phosphorescent properties at different locations were found to be within the precision of the measurements.

Comparison of spectrometers employing either an inductively coupled plasma (ICP) or a direct current plasma (DCP) was performed by Locke[40]. The ICP was generally found to be superior in glass analysis because of the higher precision associated with this source. Using an ICP (argon) source, Catterick and Hickman[41] described an atomic emission method (ICP-AES) for the

quantitative multielemental analysis of small glass fragments (200-500 μg). Samples were digested with a mixture of hydrofluoric and hydrochloric acids at ambient temperature and chromium was added as an internal standard. An ultrasonic nebulising system minimised the solution volume required for each analysis. Analysis of 200 to 500-μg glass fragments resulted in the determination of Al, Ba, Fe, Mg and Mn. Nine analyses of a sheet glass on the same day resulted in precisions of 4 to 10% (RSD) for the various elements. This rose to 10-14% (RSD) for 24 determinations made over several weeks. A more extensive survey[42,43] was conducted by the same investigators. In dealing with glasses of one particular refractive index (1.5171 ± 0.0001), eleven of twelve sheet glasses could not be discriminated on the basis of the five measured elements. They did identify, however, a sub-division of sheet glasses due to different levels of aluminum. On this basis, aluminum was believed to be a useful discriminating element for sheet glass in certain instances, with Cs, Rb, Sr and Sb probably also being beneficial for this purpose.

Hickman[44] has addressed two aspects dealing with the discrimination of sheet glass samples. He considered the selection of the best elements for discrimination and assessed the discrimination provided by a six-element ICP-AES analysis scheme for a variety of glasses covering a range of refractive index values. Four analytical techniques; ICP-AES, neutron activation analysis, flame AES and AAS; were used to study 15 colourless sheet glasses of refractive index 1.5160 to 1.5161. Of the 22 elements determined, Sr, Ba and As were found to be the most useful discriminating elements. Some discrimination was also provided by Mn, Rb, Fe, K and Li. The ICP-AES study involved the analysis of 232 samples of sheet glass spanning a refractive index

range from 1.5150 to 1.5210. Glasses within 10 narrow refractive index regions were compared with respect to Mn, Fe, Mg, Al, Sr and Ba levels. Ninety analyses, performed on a typical sheet glass during a 6 month period, resulted in relative standard deviations ranging from 8 to 15% for the six elements (200 to 500-μg fragments). At the 100-μg level these values were approximately doubled. This led Hickman to the following definition of discrimination. The ranges (average ± 2 standard deviations) of each of the elements are determined and compared for two samples. If the ranges overlap for every element then the samples are reported as indistinguishable. On the other hand, definition of two glasses as distinguishable means that the ranges for one or more elements do not overlap. The discrimination achieved by this guideline ranged from 40 (RI = 1.5188) to over 90% (RI ≥ 1.5210 or ≤ 1.5150) depending on the refractive index value considered. For refractive indices less than or equal to 1.519, the majority of discriminations arose from differences in one or two elements, while the four-, five- and six-element discriminations were more frequent at refractive indices greater than 1.519. In one of the few studies concerned with float glass, low discrimination was observed for refractive index groups containing large numbers of these glasses. In particular, the refractive index region from 1.517 to 1.519 showed an overall percent discrimination of approximately 40% for 90 glasses. Further subdivision of these glasses into three groups of 30 by cluster analysis resulted in well-defined subgroups containing predominantly float glass and a few other, chemically very similar, glasses. Discrimination within these subgroups was typically very low (0 to 6.2%) and generally only occurred when high concentrations of either Fe or Ba were present. A refractive index of 1.5210 also encompassed a large number of float glasses. Better

discrimination was found here because the compositions of these glasses showed considerable variation, suggesting several sources of manufacture.

Catterick[45] modified this sequential ICP detection system to incorporate the continuous monitoring of an internal standard (boron) by a second monochromator. Eight replicate analyses of the same window glass were performed on two separate occasions to provide sixteen separate values. For a 350-μg sample, the precision of the modified system showed an improvement of approximately 50% for Mn, Al, Sr and Ba. The improvement for Mg and Fe was 22 and 10% respectively. The resulting percent relative standard deviations for the various elements were 4.8 (Mn), 10.0 (Fe), 3.9 (Mg), 5.5 (Al), 5.5 (Sr) and 7.0 (Ba).

Koons et al.[46] studied 49 sheet glass samples using ICP-AES to determine Al, Ba, Ca, Fe, Mg, Mn, Na, Sr and Ti. Cluster analysis was employed for classification and also discrimination among glass sources. They noted during attempts to cluster a wide variety of glasses that samples made in the same manufacturing plant tended to group together. Thus, clustering offers an effective means to answer questions of discrimination or differentiation among glass sources within a sheet glass classification.

In an extensive investigation of window glass from England and Wales, Goode and co-workers[47,48] analysed for about 25 elements in 540 glass samples. Although many of the elements were determined using large sample increments, automated radiochemical separation and gamma-spectroscopy, four elements were determined using a non-destructive method -- instrumental neutron activation analysis (INAA). Aluminum, manganese, arsenic and sodium were determined in a 1-mg sample after a

one minute irradiation at a flux of 5 X 10^{12} neutrons per square centimetre per second (n cm^{-2} s^{-1}). A sodium iodide detector was employed. Simulation of three separate cases was performed by mixing one piece of each of three chosen control samples with seven pieces of glass randomly selected from the survey. By combining the information for these four elements into one criterion, only 1 out of 21 comparisons resulted in the sample being indistinguishable from the control. In each of the three cases the fragment taken from the control glass was correctly identified as indistinguishable from the control sample. Additionally, the correlation coefficients for the elements : Al, As, Ba, Ca, Hf, Mn, Na, Rb, Sb, Sc and Sr were found, in general, to be small.

In INAA, the bombardment of stable nuclei with neutrons results in the formation of radioactive isotopes whose concentrations can be measured by following the emission of gamma radiation as they decay. A convenient source of low-energy neutrons is a thermal nuclear reactor.

1.3.1 SLOWPOKE-2 Nuclear Reactor (University of Alberta)

SLOWPOKE is an acronym for Safe LOW POwer Kritical Experiment. It is a small pool type nuclear reactor developed by Atomic Energy of Canada Limited (AECL) and is designed specifically for isotope production and neutron activation analysis. Five major components comprise a SLOWPOKE-2 installation. These include a reactor, pool and control console along with irradiation and service systems. A typical installation is shown in Figure 1.3.1. Figure 1.3.2 illustrates a cut-away view of the reactor container. Included within this assembly are the core, beryllium reflectors, control rod and drive, neutron detector, thermocouple, five equispaced small irradiation tubes

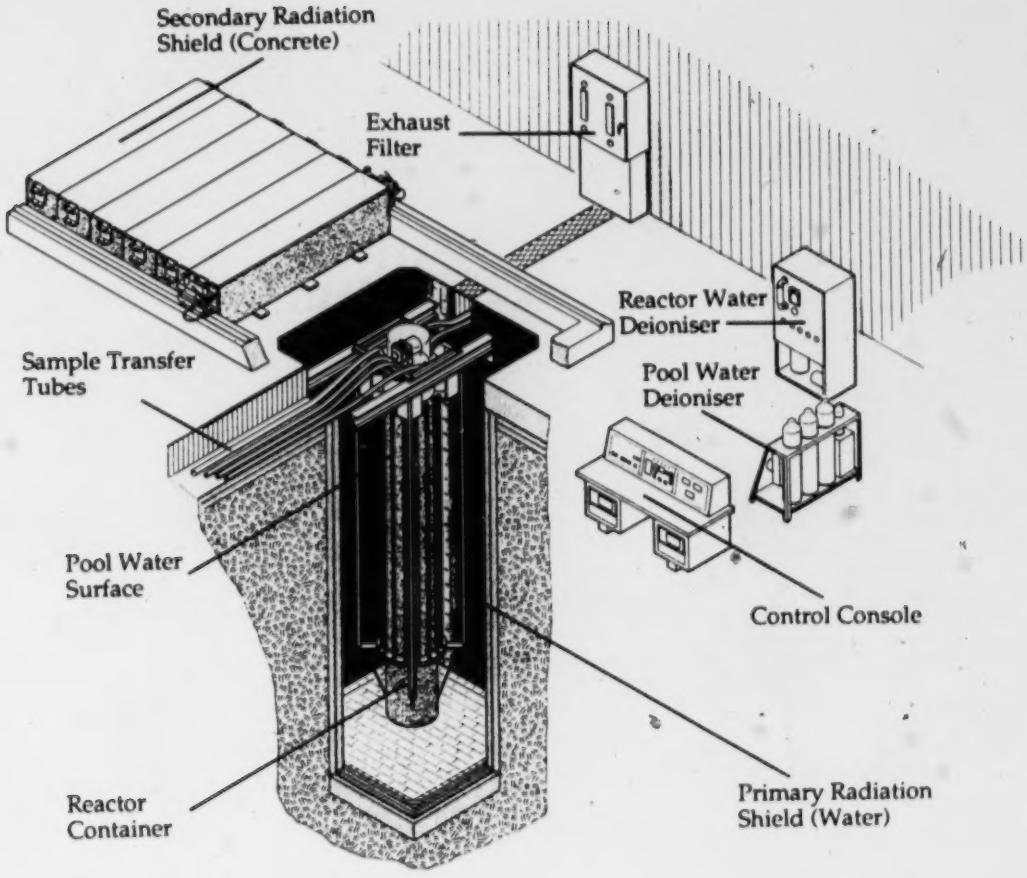

Figure 1.3.1 University of Alberta SLOWPOKE-2 Reactor Facility[49,50].

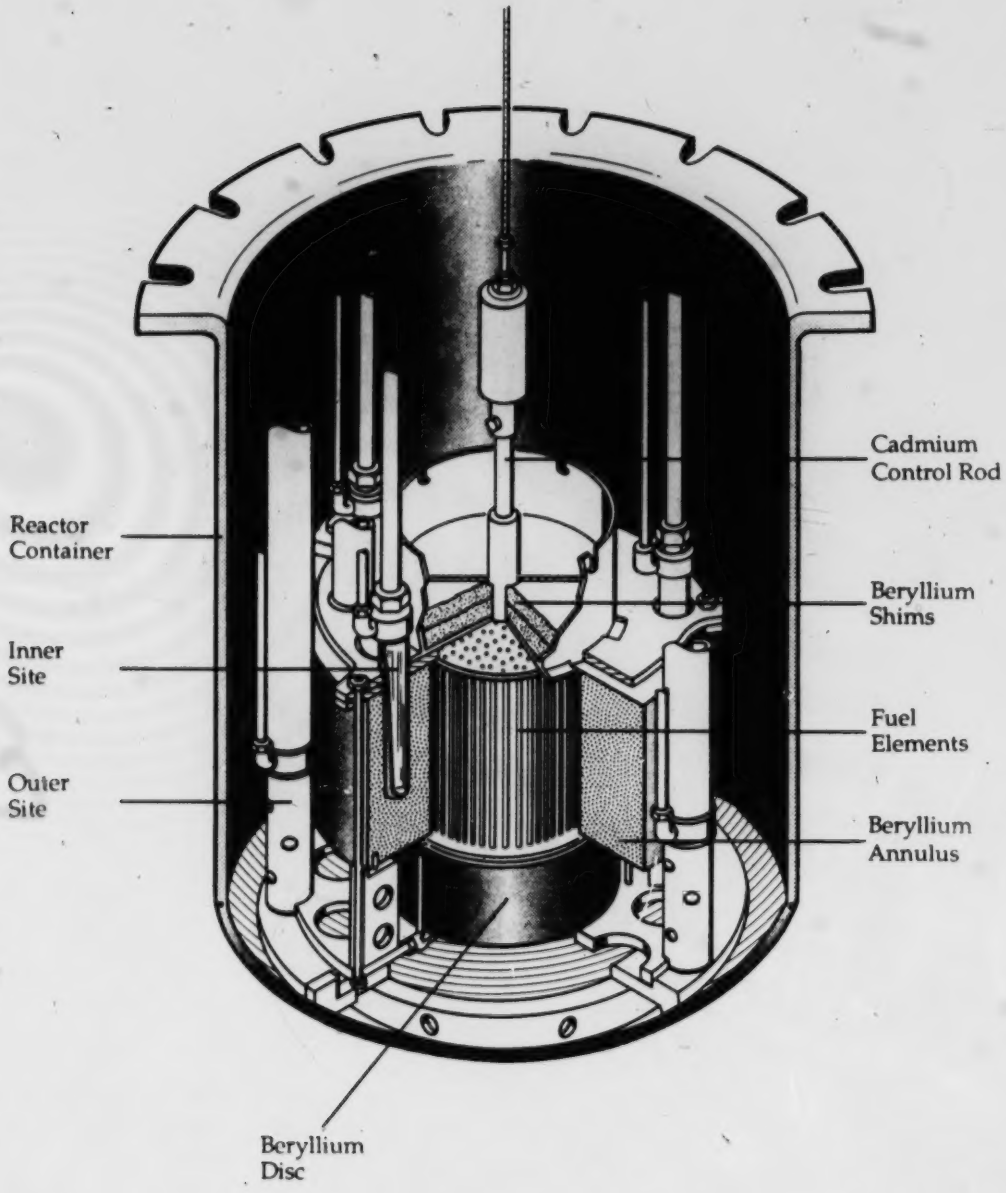

Figure 1.3.2 Cut-Away View of Reactor Container[50].

situated within the beryllium annulus (inner sites) and one large irradiation tube located outside but immediately adjacent to the reflector (outer site).

The core is 22 cm in diameter and 23 cm high and is comprised of a fuel cage and fuel elements. The cage is a spool shaped assembly of aluminum alloy containing 297 pencil-sized fuel pins. The fuel elements are ^{235}U enriched uranium-aluminum alloy, extrusion clad with aluminum. The aluminum in this case serves two functions. Its alloy with uranium permits high heat conduction within the fuel rods and thus minimises as much as possible the exposure of the fuel elements to extreme temperatures. Excessive temperatures result in damage to the fuel elements. The aluminum cladding, on the other hand, protects the fuel against corrosion and prevents contamination of the reactor water by the fuel bundle.

The fuel rods are 28% uranium (by weight) with the uranium being enriched to 93% ^{235}U (by weight). This fuel bundle, which contains only a small amount of ^{235}U, constitutes much less than the critical mass necessary to support a self-sustaining nuclear reaction. The luxury of such a small core is afforded by a beryllium reflector system, which reduces neutron loss to the surroundings and maintains an elevated thermal neutron flux in comparison to the fissile power available. This design is desirable because the consumption of ^{235}U is reduced while less shielding and cooling are required. In addition, the life of the fuel bundle is prolonged since fewer fission products with appreciable thermal neutron cross sections (poisons) are produced for a given neutron flux. In the fission process

$$^{235}U + {}^{1}n \rightarrow {}^{A1}X + {}^{A2}Y + 2.5\ {}^{1}n \qquad 1.1$$

approximately 2.5 new neutrons are released for every thermal neutron absorbed by a ^{235}U nucleus. These neutrons range in energy from below 0.1 to about 20 megaelectronvolts (MeV). The fission spectrum produced has an average energy of approximately 1.9 MeV while the most probable neutron energy is about 0.65 MeV. Sixty six percent of the neutrons have energies between 0.5 and 3 MeV and the number of neutrons above 3 MeV falls off exponentially with energy[51]. Control of the nuclear chain reaction is established by permitting only one of the new neutrons to participate in further fission events. The fission products ^{A1}X and ^{A2}Y and new neutrons result from the splitting of the ^{235}U nucleus. This process results in products having an extremely high kinetic energy. The elements produced are generally of unequal mass while approximately 200 fission products of ^{235}U have been identified[52]. The more abundant nuclear species (nuclides) include ^{95}Zr, ^{140}Ba, ^{137}Cs, ^{144}Ce and ^{99}Tc. Fission fragments are released, on average, with a kinetic energy of ~ 165 MeV, while the 2.5 prompt neutrons possess together ~ 5 MeV and the prompt γ-rays account for 7 MeV. This prompt release of energy is absorbed by the surrounding fuel bundle and reactor water.

The fast neutrons which diffuse out of the fuel elements are slowed down or moderated by materials composed of lighter elements (i.e. H_2O) that elastically scatter neutrons. Moderation maximises the probability (increases the nuclear cross section) of a fission reaction occurring. Since the moderator contains hydrogen, which is comparable in size to a neutron, transfer of energy is very efficient and therefore practically all of the kinetic energy of the neutrons is dissipated as heat. The average distance travelled by a fission neutron before reaching thermal equilibrium in water is 5.7 cm[53].

Equivalently, a 2 MeV fission neutron requires only 18 collisions with a hydrogen atom to become completely thermalised[54]. Thermalisation decreases the energy of the neutron to 0.025 eV (the most probable value at 20 °C) or a velocity of 2200 metres per second. Although the SLOWPOKE is very efficient at moderating fast fission neutrons, complete thermalisation is not achieved. Thus at any irradiation site, the flux will be predominantly thermal in nature but a significant number of fast (energies in excess of 1 MeV) and epithermal (energies between 0.55 eV and 1 MeV) neutrons will also be present. Typically, the epithermal flux at an inner site is approximately one sixteenth of the thermal flux value. Despite becoming thermalised the loss of thermal neutrons from the reactor core is still possible. Thermal neutrons are easily captured by uranium, moderator materials, fission products and impurities. In addition, a certain number of neutrons pass through the reflector and are lost.

The reactor core sits within an annular beryllium reflector while resting on a lower beryllium reflector disc. The thickness of each of these components is 100 mm. Semi-circular beryllium shims, a few millimetres thick, comprise the upper reflector. Additional shims are added over the years to compensate for fuel burn-up and poisoning, thereby maintaining a useful flux. Eventually, these poisons prevent the fuel bundle from attaining the desired flux. At this point only a few percent of the total ^{235}U present has been consumed. Correction of this situation requires either the addition of a large beryllium shim (100-mm thick) to the upper reflector or replacement of the uranium rods.

Deionised water is used both within the reactor core and the pool itself. The reactor water serves as a moderator and also provides cooling of

the core by natural convection. A thermocouple, located within the beryllium annulus, monitors the temperature of the reactor water. As a result of the reactor design any excessive heating of the fuel and reactor water results in inefficient moderation. With fewer neutrons available to sustain the nuclear reaction, the reactor power slowly decreases. This self-stabilising characteristic sets an upper limit on equilibrium power equal to the heat removal capacity of the cooling system. Heat transfer occurs through the container wall to the pool water. Since the reactor container is designed to be water tight, the integrity of the reactor and pool water is maintained. Separate water treatment systems also ensure the pool water is not contaminated. The pool is cooled by city water flowing through a simple panel heat exchanger and at no time does the city water come into contact with either the reactor or pool system. In addition, the pool system also serves as a radiation shield which may be enhanced by covering the top of the pool with several concrete slabs, approximately a metre in thickness. Operation of the reactor at a nominal thermal flux between 0.5×10^{11} and 1×10^{12} neutrons per square centimetre per second is possible. Due to the small physical size of the reactor core and the relatively high leakage of fast neutrons from the core region, the thermal neutron flux in the beryllium reflector is almost as high as at the centre of the core. The flux is limited by means of a cadmium control rod which possesses a large thermal neutron cross section. Movement of the rod in the centre of the fuel cage is guided by a tube in the shim tray. During operation of the reactor, automatic adjustment of the control rod position by a feedback mechanism that includes a self-powered flux detector maintains an approximately constant flux. The flux at a particular sample site is within ± 1/4% of the desired value with a long term reproducibility of the same magnitude[55]. In the event of a fault or failure in the cadmium control rod

network, three cadmium capsules are provided with the reactor. When placed in inner sample sites they serve as auxiliary reactor shut-down devices.

Operation of the reactor is via a control console designed as a turnkey system. The control console consists of a reactor control system, radiation monitoring system readouts and a service panel to monitor the auxiliary systems. The control system allows either automatic or manual control of the cadmium control rod position. The flux, control rod positioning and core temperature are all monitored by strip chart recorders which operate continuously. Gamma radiation detectors located above the reactor pool monitor the reactor area.

Access to the neutron flux is provided by sample transfer tubes which run into the beryllium annulus. Irradiation capsules are placed in a remote sample loading breech and are pneumatically driven by compressed air through these tubes. An irradiation controller times the irradiation. The timer starts upon a photo-detector signal which indicates arrival of the sample at the irradiation site. Upon expiry of the preset time, the sample capsule is removed and the sample is returned to a shielded lead container equipped with a radiation monitor. The air within the system is exhausted through filters to the atmosphere.

The service systems include water purification, cooling and gas purging facilities. Pool water is passed through a carbon filter followed by anion and cation exchange resins. A mixed bed deioniser is used to treat the reactor water. A gamma-ray monitor mounted near the ion exchange columns warns if fission products escape from defective fuel rods. Hydrogen, produced by the radiolytic decomposition of water, slowly builds up in the reactor container

head space. To prevent the build-up of explosive amounts of hydrogen, purge air is blown through the head space once per week. The purge air is filtered before being exhausted to the atmosphere.

1.4.1 Radioactivity and Its Detection

The inelastic collision of a low energy neutron and a nucleus, with the prompt emission of electromagnetic radiation (γ-rays), constitutes neutron capture. For example,

$$^{39}K + {}^{1}n \rightarrow {}^{40}K + \gamma_{prompt} \qquad 1.2$$

results in the formation of an energetic isotopic product containing an extra neutron. To reach an energetically stable state, this product must release its excess energy either as kinetic energy of the products of a further nuclear reaction (α– and β-decay), electromagnetic radiation (γ-rays), or both. Beta decay, by far the most common of all these processes, encompasses negatron emission (β^- or e^-), positron emission (β^+ or e^+) and electron capture reactions.

An example of negatron decay can be written as

$$^{40}K \rightarrow {}^{40}Ca^+ + \beta^- + \nu' \qquad 1.3$$

where the radioactive product possessing an additional proton is accompanied by the release of an electron (β^-) and an antineutrino (ν'). In this reaction ^{40}K may be viewed as having an over-abundance of neutrons. Reduction of this neutron excess is accomplished by conversion of a neutron to a proton. Therefore, β^--decay may be viewed simply as

$$^{1}n \rightarrow {}^{1}H^+ + e^- + \nu' \qquad 1.4$$

where the creation of an electron happens at the instant it is emitted from the nucleus. As shown by equation 1.3, β^--decay characteristically converts an odd (neutron number) - odd (proton number) nuclide to an even - even nuclide. An excessive proton to neutron ratio results in positron decay. This decay mode

$$^{40}K \rightarrow {}^{40}Ar^- + \beta^+ + \nu \qquad 1.5$$

produces a radioactive product with one less proton, a positron and a neutrino (ν). The presentation of positron decay may also take the form

$$^{1}H^+ \rightarrow {}^{1}n + e^+ + \nu \qquad 1.6$$

Electron capture competes with positron decay for the reduction of the proton to neutron ratio. In capturing an electron from an inner orbital of the atom, a proton in the nucleus is converted to a neutron

$$^{40}K + \beta^- \rightarrow {}^{40}Ar^- + \nu \qquad 1.7$$

or

$$^{1}H^+ + e^- \rightarrow {}^{1}n + \nu \qquad 1.8$$

For neutron deficient nuclei with proton values less than 30, positron emission dominates, while electron capture primarily occurs for nuclei with atomic numbers greater than 80[56]. Between these extremes, the two processes compete to varying degrees.

An inelastic collision between a neutron and a target nuclide may also result in the release of a charged particle. The charged particle is commonly a proton but other particles (e.g. α-particles, $^{4}He^{2+}$, and deuterons, $^{2}H^{+}$) may be

released. Most of these reactions have a threshold energy associated with them and, therefore, only occur with neutrons possessing energies well above those of thermal neutrons.

Following α- and β-decay, the product nucleus is frequently left in an excited state. This excitation energy is removed either by γ-ray emission or by a process called internal conversion. In the great majority of cases the emission of a γ-ray occurs immediately (i.e. within approximately 10^{-12} seconds) after α- or β-decay. However, in some instances the nucleus may remain in a higher energy state (metastable state) for a finite period of time. Such longer-lived excited nuclei are called isomers. Internal conversion competes with γ-ray emission as an alternate mode for the release of nuclear excitation energy. The internal conversion process occurs because the wave function of an orbital electron overlaps that of the excited nucleus. As a consequence, the excitation energy of the nucleus is transferred directly to the orbital electron, causing it to escape from the atom with a certain kinetic energy. The ejected electron, known as the conversion electron, normally originates from an inner orbital since inner orbital wave functions have a greater overlap with the nucleus. Generally, γ-ray emission is at least a factor of ten more prevalent than internal conversion[57].

The detection of γ-radiation is made possible by its interaction with matter (detector). As a result of this interaction, a discrete amount of energy is exchanged. Gamma-ray detection may occur by any of the following four processes : coherent scattering, photoelectric and Compton effects and pair production. In coherent scattering, absorption of a γ-ray is followed by its immediate re-emission from an atom. The γ-ray is unchanged in energy but leaves in a different direction from its initial approach. Coherent scattering

increases with the square of the atomic number of the absorber and decreases with γ-ray energy. Complete absorption of a γ-ray, with subsequent excitation and ejection of orbital electrons from the detector material, is referred to as the photoelectric effect. Since an inner orbital electron is often ejected, this [illegible] is generally accompanied by the emission of X-rays and low energy Auger electrons. The probability of the photoelectric effect decreases with increasing γ-ray energy and is largest for inner shell electrons. In the Compton effect, a high energy gamma-ray interacts directly with a valence electron. The electron is ejected and the resulting lower energy γ-ray is deflected. Even though the scattered gamma-ray may still possess sufficient energy to interact further by the Compton, photoelectric or pair production effects, it generally escapes without detection. Again, the emission of X-rays and Auger electrons usually accompanies a Compton interaction. Compton scattering increases with the atomic number of the target and is important for γ-rays with energies between 0.5 and 5 MeV. Pair production involves the conversion of a gamma-ray into an electron and a positron by interaction with the electrostatic field of a nucleus. Since the rest mass of an electron corresponds to 0.511 MeV, the γ-ray must have a minimum value of 1.022 MeV to interact by pair production. Any excess energy beyond this value appears as kinetic energy of the pair. The probability of pair production increases as the energy of the γ-ray increases beyond 1.022 MeV and predominates when the γ-ray energy is greater than 5 MeV. Upon losing its kinetic energy, a positron will interact with an electron in the detector. The annihilation of both particles results in the production of two 0.511-MeV photons. This radiation is then absorbed by the processes described above. Pair production will occur more frequently with increasing atomic number of the absorber and decreasing γ-ray energies.

Solid-state or semiconductor detectors are commonly employed in gamma-ray spectroscopy. In effect, they convert the energy of a γ-ray into an electrical signal. By incorporating a small quantity of a Group IIIA element into a germanium block, a p-type semiconductor is obtained. The diffusion of lithium into one surface of this block, followed by the application of a reverse bias voltage, creates a charge-depleted or intrinsic region. Cooling of the detector block to the temperature of liquid nitrogen further limits the current flow in this high resistivity region and creates an effective volume where any detected current must be the result of an interaction between a γ-ray and the detector. The average energy required to produce an electron-hole pair in a germanium semiconductor is 2.98 eV[58] at 77 °K. As a result of this low threshold energy, better resolution and counting statistics are possible. After ionisation, the electrons are swept from this region towards the positive electrode along with any secondary electrons produced from further ionisation processes. Ideally, the charge pulse collected at the positive electrode is proportional to the energy lost by the incident photon upon interaction with the detector. Recently, hyperpure germanium crystals (intrinsic detectors) with impurity levels below 1×10^{10} per cubic centimetre[59] have been produced. At such low impurity levels, lithium drifting is no longer necessary. However, cooling of the detector to liquid nitrogen temperature (77 °K) is still required since mobile carriers are present at room temperature.

Further processing of the detector signal requires several stages. The preamplifier augments and conditions the detector signal and outputs a step voltage that can be easily processed by conventional amplifiers and multi-channel analysers. Multiplying these output pulses by a constant factor while

maintaining the linear relationship between them is the function of the amplifier. Additionally, it also shapes the voltage pulses which permits their subsequent analysis by means of pulse height analysis routines. Shaping of these pulses is not trivial and several special circuitry features are necessary to ensure the integrity of this process. Pole-zero cancellation and base-line restoration are commonly employed to prevent distortion of the peaks in a spectrum. The amplification function can be expressed in a mathematically simple form

$$V_{out} = k \times V_{in} \qquad 1.9$$

where the input and output voltages of the amplifier are represented as V_{in} and V_{out} respectively. The constant factor, k, is called a gain function. In the frequency domain, equation 1.9 becomes

$$V_{out} \approx k' V_{in} / (1 - 2\pi f/RC) \qquad 1.10$$

with f being the frequency, R and C the resistive and capacitive elements in the circuit and k' is now a new constant. When the frequency equals $RC/2\pi$ a singularity, called a pole, occurs. However, by including a feedback resistor in the amplifier circuit this event may be circumvented by forcing the output voltage to zero when a pole arises. Baseline restoration ensures that all peak height measurements are taken relative to a reproducible baseline.

Very high counting rates may also distort the analytical spectrum. Two distinct events (γ-rays) may occur so close together in time that only their combined event will be analysed and processed. This effect is termed pulse pile-up and results in the loss of counts at a particular energy. Correction of this distortion is possible by placing a pulser in the detection circuit. Since the

number of these combined events is independent of spectral location, the pulser is generally located away from any spectral areas of interest. The pulse pile-up correction factor is obtained by counting the pulser in the absence and presence of a sample, i.e.

$$\text{Correction Factor} = \text{pulser counts}_{no\ sample} / \text{pulser counts}_{sample} \quad 1.11$$

Multiplication of all the peaks in a spectrum by this factor leads to correction of the pulse pile-up effect.

The voltage output from the amplifier is then passed to a multi-channel analyser (MCA). This device consists of an analog-to-digital converter (ADC) along with memory, display and input/output functions, all under the control of a central processing unit (CPU). After the successive approximation ADC converts the pulse height of the detector (analog) signal into a channel number (digital signal), the CPU increments the appropriate memory location corresponding to the particular photon energy. This information is then relayed via input and output circuitry and the external display is updated. Throughout this detection procedure, system noise (primarily due to the preamplifier) and the randomness of electron-hole pair production within the detector produce variations in the pulse height for photons of the same energy. This results in the generation of a photopeak spread over several channels. The features associated with a typical γ-ray spectrum are presented in Figure 1.4.1.

An MCA requires a finite interval of time to process each analog signal into its digital equivalent. As a consequence, there will be a certain period of time during the total counting interval in which the MCA will be unable to accept any charge pulses. This time is referred to as the dead time (DT) of the

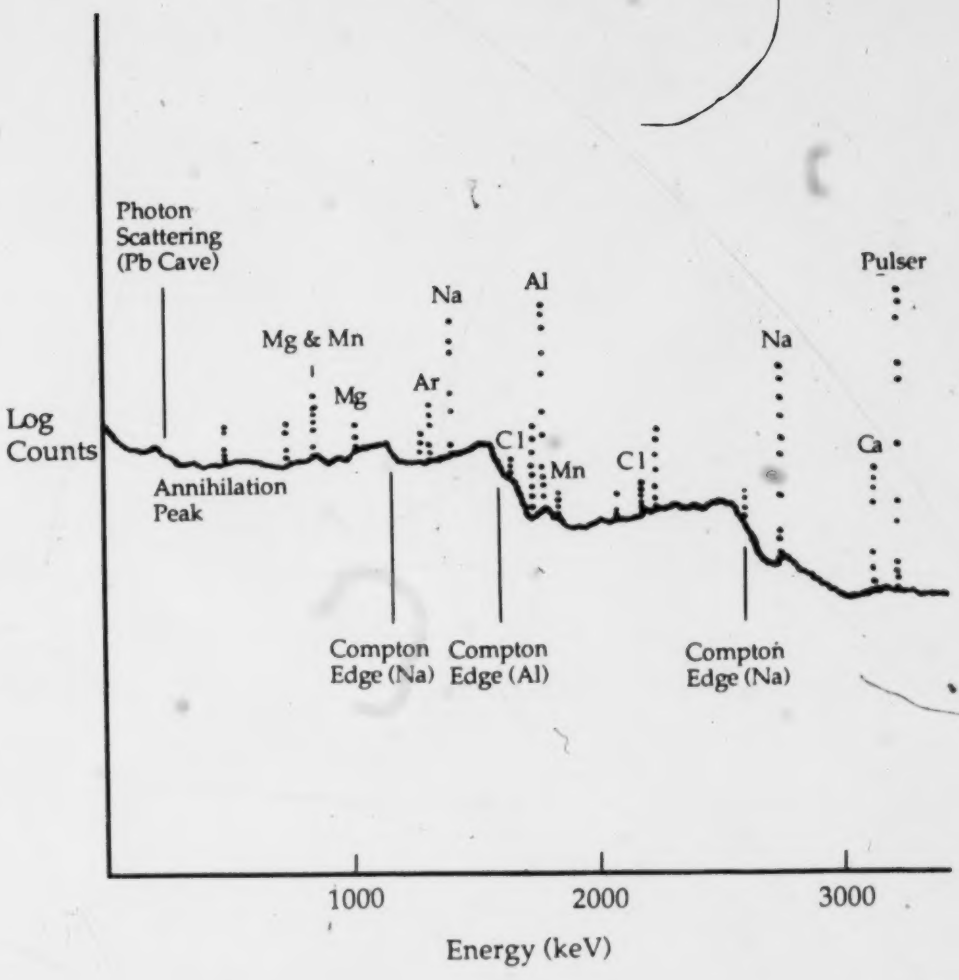

Figure 1.4.1 Typical 4096 Channel γ-Ray Spectrum of Soda-Lime Glass After Irradiation at 1 X 10^{12} n cm^{-2} s^{-1} For 240 Seconds, Hyperpure Germanium Detector. Unlabelled photopeaks result from pair production.

analyser. The addition of the live time (LT) to this dead time results in the determination of the total elapsed clock time (CT) for the detector. Since different spectra will have different dead times associated with them, comparison of the photopeak intensities obtained by MCA counting can only be performed after a so called live time - dead time correction factor is taken into account. Its determination will be outlined here for the situation where counting of a short-lived radionuclide occurs in the presence of a long-lived or essentially constant background. The fractional dead time (FDT) may be defined as follows :

$$FDT = DT/CT = (CT-LT)/CT \qquad 1.12$$

Assuming a FDT of zero (CT = LT), the total number of counts c, observed for a given clock time are

$$c = A^\circ [1 - \exp (- \lambda LT)] \qquad 1.13$$

where A° is a constant for a particular counting period and λ is the decay constant. The following relationship exists between the decay constant and the radioactive half life ($t_{1/2}$) of a nuclide.

$$\lambda = \ln 2 / t_{1/2} \qquad 1.14$$

In practice, however, the dead time will be greater than zero and integration from zero to CT will be necessary. Since only a fraction of the possible counts are recorded, multiplication by the fraction (LT/CT) is also required. These last two statements are true provided the source (background + radionuclide of interest) is not decaying appreciably during the counting period. If this requirement is met, the number of counts actually recorded are

$$c' = A^{\circ} [1 - \exp(-\lambda CT)] (LT/CT) \qquad 1.15$$

Multiplication of the various photopeaks by the factor

$$c/c' = \{ [1 - \exp(-\lambda LT)] / [1 - \exp(-\lambda CT)] \} (CT/LT) \qquad 1.16$$

results in correction of the spectra to zero dead time, hence, permitting the comparison of photopeaks from different spectra.

1.4.2 The Application of Statistics to Radioactive Decay Processes

Radioactive decay is best described in statistical terms due to its random nature. This uncertainty in the decay process results in a different number of counts being obtained when the same sample is counted over a similar interval of time. Consequently, the decay of a radioactive nucleus within any one time interval may only be assessed a certain probability. If this counting of the same sample is repeatedly performed, a distribution of counts about a central point (population mean) is obtained. This distribution is correctly expressed by the binomial distribution law and permits calculation of the probability that any recorded number of counts is within certain limits of the population mean. Generally, the much simpler Poisson distribution or the Gaussian (normal) distribution functions are used. If the average number of counts is high (above 100) the Gaussian function may be used with no appreciable error[60]. In the Gaussian case, the probability of observing N counts is

$$P(N) = \{1 / (2 \pi N)^{1/2}\} (\exp - [(N - N_{ave})^2 / 2N]) \qquad 1.17$$

where the standard deviation σ is given by $\sigma = N^{1/2}$, there are N measured counts and N_{ave} is the average of all these values. From the relationship

between σ and N, it follows that the greater the number of collected counts, the smaller the uncertainty. As shown in Figure 1.3, the photopeaks of most spectra are associated with an underlying background. In this situation, the net photopeak area (A) is obtained by finding the total area under the peak (i.e. the net photopeak area + background counts) and subtracting the underlying background counts (B). If error propagation is performed, the uncertainty (standard deviation) associated with this quantity is found to be $(A+2B)^{1/2}$. This quantity is commonly known as the statistical uncertainty associated with an analysis.

1.5.1 Research Definition

The focal point of this research centres around the discrimination by instrumental neutron activation analysis methods of flat glasses found within the same refractive index group. The research goal was to compare and contrast various flat glass samples, randomly selected from a glass population, under carefully controlled experimental conditions. To accomplish this objective, inquiry into the elemental composition of each glass was deemed necessary. A non-destructive technique was required to preserve for court evidence the small amount of material that is often obtainable from a suspect. For this reason, instrumental neutron activation analysis was selected as the analytical method of choice. A further restriction was that only short irradiation, delay and count times were considered because of the need for relatively rapid analytical turn around times. In addition to the preceding objective, the investigation of small sample increment sizes was also of interest. This concern with small sample sizes,

immediately called into question the distribution profile of the various elements within these glasses.

Chapter 2

Introduction

2.1.1 Background

Experimentation, in general, involves the collection of measurements from a system of interest. Ideally, only random errors will be associated with this process. Random errors will be present since it is impossible to directly control all the potential variables in a particular experiment. As a result, individual measurements will tend to be distributed both above and below a central value with approximately equal relative frequency. Statistics and probability are the branches of mathematics devoted to the scientific study of this random phenomena. They concern themselves, respectively, with inductive and deductive reasoning. Inductive reasoning involves extrapolation from a small number of measurements (i.e. the sample) to the expected result if repeated and exhaustive sampling were performed (i.e. the population distribution). An important precondition for inductive reasoning is that some randomness exists in the sampling process. Random sampling ensures that each member of the population has an equal chance of being included in the sample and hence prevents sampling bias from adversely affecting any inferences about the underlying population. Since the validity of many standard statistical procedures relies on this property, random sampling is a very important concept in statistics. Starting from a specified population, deductive reasoning makes predictions about the resulting sample. This

deductive field is the attention of probability. The binomial, Poisson and Gaussian (normal) distributions are commonly encountered.

Statistical inference theory generally assumes that the observations X_1, X_2, ... , X_n are values of random variables x_1, x_2, ... , x_n (i.e. different values for the sample may be obtained on different days) that are independent and each of the x_i (i=1 to n) has a common normal distribution. If this normality assumption is true, μ and σ^2 denote the mean and variance of any one of the x_i (this is written as $x_i \sim N(\mu, \sigma^2)$, i=1 to n). It can be shown that the sample average, x_{ave}, defined by

$$x_{ave} = (1/n)(x_1 + x_2 + \ldots + x_n)$$

$$= \sum x_i/n \qquad 2.1$$

where n is the total number of measurements and the symbol Σ is a short-hand mathematical notation for the summation from i=1 to n, is normally distributed with mean, μ, and variance, σ^2/n (i.e. $x_{ave} \sim N(\mu, \sigma^2/n)$). Even if the x_i do not have a normal distribution, then $x_{ave} \simeq N(\mu, \sigma^2/n)$ where " $\simeq$ " means "approximately distributed as", if n is large. This is the Central Limit Theorem. In practice, it is not clear how large n should be before an approximately normal distribution for x_{ave} may be assumed. Statistical texts will typically state $n \geq 30$ while some non-parametric procedures use $n \geq 15$. The required n depends on the actual distribution of the x_i and the degree of closeness to normality that is required.

In chemical experiments, individual random observations may each be assumed to have a distribution which is not too discrepant from normality. Hence, even for quite small n, x_{ave} will be close to normal. This same

argument is used to assume (see section 2.3.3) that random error variables in experiments generally have normal distributions, in fact N $(0, \sigma^2)$.

2.1.2 Confidence Intervals

The probabilistic result

$$x_{ave} \sim N(\mu, \sigma^2/n) \qquad 2.2$$

can be used in statistical theory to make inferences about an unknown μ. Equation 2.2 can be re-written as

$$(x_{ave} - \mu) / (\sigma/n^{1/2}) \sim N(0, 1) \qquad 2.3$$

By consulting tables of the standard normal distribution (i.e. N (0, 1)) for any number α, where $0 < \alpha < 1$, it is possible to find a number $z_{\alpha/2}$ to satisfy

$$P(-z_{\alpha/2} < (x_{ave} - \mu) / (\sigma/n^{1/2}) < z_{\alpha/2}) = 1-\alpha \qquad 2.4$$

This is the same as

$$P(x_{ave} - (z_{\alpha/2} * \sigma/n^{1/2}) < \mu < x_{ave} + (z_{\alpha/2} * \sigma/n^{1/2})) = 1-\alpha \qquad 2.5$$

where 100 $(1-\alpha)$% of the random intervals $(x_{ave} - (z_{\alpha/2} * \sigma/n^{1/2}))$, $(x_{ave} + (z_{\alpha/2} * \sigma/n^{1/2}))$ will contain the unknown μ. When a particular X_{ave} is observed (i.e. the observed value of the random variable x_{ave}), a confidence of 100 $(1-\alpha)$% may be stated that the interval $X_{ave} \pm z_{\alpha/2} * \sigma/n^{1/2}$ contains μ. However, the standard deviation of each of the random variables $x_1, x_2, \ldots, x_n$ (i.e. the population standard deviation, σ) is generally unknown. Replacement of σ by s, the standard deviation of the sample,

$$s = (\sum (X_i - X_{ave})^2/(n-1))^{1/2} \qquad 2.6$$

and $z_{\alpha/2}$ by $t_{\alpha/2}$, obtained from tables of the t-distribution with n-1 degrees of freedom, results in the interval $X_{ave} \pm t_{\alpha/2} * s/n^{1/2}$ being a 100 (1-α) % confidence interval for μ.

2.1.3 Hypothesis Testing

Equation 2.2 can also be used for other statistical inferences, such as hypothesis tests about μ. Generally, a null hypothesis, $H_0 : \mu=\mu_0$ (where μ_0 is a specified value of μ) will be rejected in favour of an alternative hypothesis $H_1 : \mu\neq\mu_0$ if

$$\left|(X_{ave} - \mu_0) / (s/n^{1/2})\right| > t_{\alpha/2} \qquad 2.7$$

It can be shown from equation 2.2 that the random variable $(x_{ave} - \mu_0) / (s/n^{1/2})$ has, if H_0 is true, a t-distribution with n-1 degrees of freedom.

Often in hypothesis testing, a probability value or an observed level of significance is computed for a test. This means, given the data $X_1, X_2, \ldots, X_n$, the probability under H_0 is computed (assuming H_0 true) of getting a value of $(x_{ave} - \mu_0) / (s/n^{1/2})$ at least as extreme as the value actually observed $(X_{ave} - \mu_0) / (s/n^{1/2})$. If this probability is smaller than some pre-assigned number α (called the level of significance - generally 0.01 or 0.05) H_0 is rejected in favour of H_1. The sample result is said to be statistically significant, meaning that the sample average differed significantly from the hypothesized value μ_0. This also signifies that there was too small a probability of observing such an extreme value of x_{ave} prior to sampling that the validity of the null hypothesis must be questioned. Any future discussion of this matter will use the term statistically discernible difference in place of statistically significant.

Rejection of the null hypothesis is also important because one can never be entirely certain that the correct decision has been made. This has led to the introduction of an error concept in statistics. In hypothesis testing, it is entirely possible to obtain a value of a sample statistic that exceeds the (e.g. 5%) significance level of a test simply based on random error alone. The probability of such an occurrence, in this particular case, is on average 5 out of 100 trials. As a result, an extreme value may be incorrectly rejected. This is commonly referred to as a type I error. On the other hand, a type II error arises when the null hypothesis is not rejected when in actual fact it should have been rejected. Thus, a type II error expresses the proportion of samples from the population represented by the alternative hypothesis, H_1, that fall within the acceptance region of the null hypothesis. In the above statements, the phrase "accepting the null hypothesis" has been carefully avoided. This acknowledges the fact that the sample and hypothesized distributions may actually be different but the random error associated with the measurement process obscures this difference.

A practical example[61] will now be presented to more clearly illustrate the concept of error in statistics. In legal trials, a jury is asked to decide between H_0, the hypothesis that the accused is innocent, and H_1, that he is guilty. If an innocent man is condemned, a type I error is committed whereas if a guilty man is set free a type II error results. By admonishing the jury that, "guilt must be proved beyond a reasonable doubt", the judge means that the type I error should be kept very small. However, by reducing the chance of convicting an innocent man (a type I error) it is impossible to prevent the type II error from increasing (the probability that a guilty man will evade punishment) for a fixed sample size. In this particular case, a type I error is

deemed to be the more serious of the two and thus the testing procedure takes this into account by controlling this error. Careful control of type I error is a common occurrence.

While the t-statistic is especially useful for comparing a single sample average to a population mean, and another t statistic is available for two-sample problems, the F-test is routinely employed for the comparison of three or more averages. The F-test compares the variance between different data sets to the variance within these sets. This is expressed mathematically as

$$F = \text{Mean Square}_{between} / \text{Mean Square}_{within}$$

$$= (n/(r-1))\Sigma(X_{ave} - X_{ovave})^2/(1/r(n-1))\Sigma\Sigma'(X_{ij}-X_{ave})^2 \qquad 2.8$$

where there are r data sets and n observations in each set, X_{ovave} is the overall average or the average of the r data set averages, X_{ave} are the data set averages, X_{ij} are the individual observations within the data sets, Σ is the summation from 1 to r and Σ' is the summation from 1 to n. The numerator of this expression reveals the variation that may arise from the presence of populations whose means are not all equal while the denominator accounts for the total random variation. Once again the testing of means may be performed and the probability that various samples have a common mean may be determined. Critical F-values may be obtained from tabulations by looking under the appropriate degrees of freedom associated with the numerator and denominator. If the calculated F-value is larger than the critical F-value, the conclusion drawn is that at least one of the tested means is statistically discernible from the remaining means. To find out which mean differences are discernible requires the performance of multiple comparisons. Several methods to perform this task have been proposed. Two tests which

are commonly used are the least statistically discernible difference (LSDD) and Tukey's alternate multiple comparisons procedure (Tukey B).

2.1.4 Multiple Comparisons Procedures

The least statistically discernible difference method examines the difference between each pair of means in a planned comparisons test. Planned comparisons refers to the circumstances where the comparisons to be studied are determined prior to inspection of the results of the variance analysis. In this test, the t-statistic takes the following form

$$t_s = (X_{1,ave}-X_{2,ave})-(\mu_1-\mu_2) \;/\; \{(1/n_1+1/n_2) * \text{Mean Square}_{within}\}^{1/2} \qquad 2.9$$

and when $n_1=n_2$ (i.e. equal sample sizes)

$$t_s = (X_{1,\,ave}-X_{2,\,ave})-(\mu_1-\mu_2) \;/\; (2/n * \text{Mean Square}_{within})^{1/2} \qquad 2.10$$

Although in any one specific test fewer observations may be involved than in the full analysis of variance, the number of degrees of freedom (υ) is based on the $\text{Mean Square}_{within}$ term. This is in contrast to the t-test discussed previously. Assuming that $\mu_1-\mu_2=0$ and $t_s=t_{\alpha[\upsilon]}$, equation 2.10 may be rearranged

$$X_{1,\,ave}-X_{2,\,ave} = t_{\alpha[\upsilon]} * (2/n * \text{Mean Square}_{within})^{1/2}$$

$$= \text{LSDD} \qquad 2.11$$

where $X_{1,\,ave}-X_{2,\,ave}$ represents the difference that will just be sufficient to result in a statistically discernible result between any pair of means, in an equal sample size study at a probability α (type I error), when substituted in equation 2.11. Thus, the calculation of an LSDD permits a quick method for

the comparison of any pair of means to test for a discernible difference. The type I error for this procedure is a pairwise error, which indicates that it is applicable to every comparison performed. As a consequence, if several pairwise multiple comparisons are performed in the analysis of an experiment, the chance of making a type I error in any of the comparisons becomes substantial. In contrast, an experimentwise error rate ensures that the chance of making any type I error in the total number of comparisons required for an experiment will not be above a specified level. The experimentwise error includes both the overall test (F-test) and any of the subsidiary comparisons among means or sets of means needed to complete the analysis of the experiment. The tests performed will be somewhat insensitive (i.e. conservative) to differences between individual means or differences within small subsets. This conservatism arises since the error rate for each individual test will be a fraction of the overall experimentwise error rate.

Tukey's alternate multiple comparisons procedure[62-64] employs an experimentwise error rate. The procedure may be generalised as

$$\text{MSDD} = \text{critical value} * \text{SE} \qquad 2.12$$

where MSDD represents the minimum statistically discernible difference, the critical value refers to the statistical distribution appropriate for the given test and SE is the standard error of the difference in means. The studentized range, $Q_{\alpha[k,\,\upsilon]}$, is the critical value employed in the Tukey B procedure. The critical values are obtained for the distribution of range/$s_{x,\,ave}$ for k means, each normally distributed, where $s_{x,\,ave}$ is an estimate of the standard error of

these means. A minimum statistically discernible range (MSDR) employing the studentized range may be defined as

$$MSDR = (Q_{\alpha[k,\,\upsilon]} + Q_{\alpha[p,\,\upsilon]})/2 * (\text{Mean Square}_{within}/n)^{1/2} \qquad 2.13$$

where p = (the rank of the larger mean minus the rank of the lower mean plus 1). The above equation is analogous to equation 2.11 since the 2 inside the square root in 2.11 has been incorporated into the Q-value. In practice, the group means are placed in ascending order, i.e. ranked, as

$$X_{1,\,ave} \leq X_{2,\,ave} \leq X_{3,\,ave} \leq \ldots \leq X_{(k-1),\,ave} \leq X_{k,\,ave} \qquad 2.14$$

and $X_{k,\,ave}$ is successively compared with $X_{1,\,ave}$, $X_{2,\,ave}$ and so on until the difference in the means is less than the critical value (i.e. MSDR). If ($X_{k,\,ave}$-$X_{1,\,ave}$) is not statistically discernible, the test ends, since no standardised subset range can exceed the critical value unless ($X_{k,\,ave}$-$X_{1,\,ave}$) does. If the testing procedure continues, the means found to be statistically discernible from $X_{k,\,ave}$ are tested against $X_{(k-1),\,ave}$, again starting with $X_{1,\,ave}$. All means found to be statistically discernible from $X_{(k-1),\,ave}$ are tested against $X_{(k-2),\,ave}$ and so on until no further statistically discernible difference can be obtained. In the Tukey B procedure, all of the k(k-1)/2 comparisons are included in determining the experimentwise error.

Although the above statistical procedures are specifically for univariate data (i.e. where one variable is compared between data sets) each procedure has a multivariate analogue. The multivariate procedures consider the global, or cumulative, response which is composed of the different variables involved in the analysis scheme. Thus, a multivariate response may be viewed as a vector in w-dimensional space where each of the dimensions

corresponds to the level of, for example, a particular element in the glass of interest. A simple example would involve the Euclidean distance between two mean vectors. Once again, if the distance is greater than some critical distance, then the two mean vectors, each consisting of several variables, would be deemed statistically discernible.

Experimental Details

2.2.1 Refractive Index Measurements and Observations on Nineteen Glass Samples

Nineteen glass samples comprising five refractive index (RI) groups were obtained from a Royal Canadian Mounted Police (RCMP) forensic laboratory (Edmonton, Alberta). Sample presentation typically ranged anywhere from a few milligrams of crushed glass to fifty grams of a complete section of glass. Thicknesses ranged between 2.8 and 6 millimetres. Refractive index measurements were performed with a Mettler FP52 hot stage (MSE Scientific Instruments, Crawley, Sussex, England), coupled to a Glass Refractive Index Measurement (GRIM) control unit[65], with silicone oil B (n_D = 1.537 at 20 °C and n_D = 1.520 at 65 °C, Locke Scientific, 16 Oakfield Rd., Pamber Heath, Basingstoke, Hampshire, England) serving as the immersion medium. These measurements were reported for the mean value of the doublet sodium D line (589.3 nm) at a temperature of 25°C and the overall uncertainty associated with the method was ± 0.0001 RI units. The refractive index measurements and the classification of each glass were provided by the local authorities. Table 2.2.1 provides general information on the various glasses. All were clear except for sample A2, which was slightly greenish, and E2, which was smoke coloured. Where not explicitly stated in Table 2.2.1, only

Group	n_D	Glasses In Group	Glass Classification	Observations
A	1.5171	4	A1, A3, A5 - flat A2 - flat, safety (car window)	A2 - slight greenish tinge, 2 pieces plus small shards A5 - 3 pieces
B	1.5185	4	B1 - tableware (tumbler) B2, B3, B4 - flat	B3 - crushed glass sample
C	1.5157	3	C1, C2 - flat C3 - flat, safety (tempered)	
D	1.5168	4	D1 - flat, safety (tempered) D2, D3, D4 - flat	
E	1.5191	4	E1, E3 - flat E2 - flat (decorative) E4 - flat (windshield)	E2 - smoke coloured, 2 pieces E4 - 2 glasses, laminated together and each 3 mm in thickness

Table 2.2.1 Physical Properties, Classification and Observations Involving Glass Fragments Provided by the RCMP. All glasses not indicated otherwise were provided as a single piece.

one intact piece of glass was provided. Each glass in the set was subsequently observed under short-wave ultraviolet (UV) radiation in a UV light box (Chromato-Vue, Ultra-Violet Products, Inc., San Gabriel, California, U.S.A.) to test for fluorescence.

2.2.2 Sample Pretreatment

Large pieces of glass were placed between a double thickness of paper and crushed, using a hammer. Portions of the original samples were further crushed using an agate mortar and pestle equipped with a Parafilm "M" (American Can Company, Greenwich, Connecticut, U.S.A.) cover. The resulting fragments were less than 1 millimetre (mm) in maximum dimension. The crushed samples were then placed in clean 30 X 65 mm glass vials (Kimble Company, Division of the Owens-Illinois Glass Company, U.S.A.) and cleaned with concentrated nitric acid for 30 minutes. Washing of the samples with distilled-deionised water was performed three times prior to a 95% ethanol rinse. The samples were then dried in a National Appliance Company, Model 5851, vacuum oven between 100 and 110°C for at least 4 hours. Drying was performed just prior to weighing the samples.

2.2.3 Subsample Preparation

Increments of nominal mass 1 mg and 100 µg were taken from each glass sample for analysis by INAA. The actual subsample increments were in general within 10% of the nominal value. A Cahn Gram (Model G, loop A and 1-mg range setting) Electrobalance (Cahn Instrument Co., Paramount, California, U.S.A.), equipped with powder paper (glassine) pans, was employed to weigh out four subsamples at each increment level. The

subsamples were then placed directly into four nitric acid washed (25% volume/volume) 400-µL polyethylene micro-centrifuge tubes (Beckman Microfuge Tubes) which had been previously cut in half crosswise. Care was taken to avoid skin contact with the micro-centrifuge tubes. These tubes were capped, heat sealed on the edges of the cap (AECL commercial products, Model #K9-044), placed in 1-mL polyethylene vials and finally inserted into 7-mL polyethylene irradiation vials. The 1- and 7-mL polyethylene containers were produced by Olympic Plastics Company, Inc., Los Angeles, California, U.S.A.. Empty, 1-mL polyethylene vials, acting solely as spacers, were placed on top of the 1-mL polyethylene vials containing the subsample already present in the irradiation tubes. All subsamples were analysed in triplicate, with one week separating each analysis to allow for decay of the various radioisotopes. One blank (polyethylene sample tube plus vials) was also analysed daily for each sample increment level. The analysis of the blanks served solely to monitor the counting operation for any gross contamination or unusual background fluctuations, since low blank levels made blank correction of the subsample values unnecessary. Irradiation and counting of the various subsamples was performed using a randomised block design. In this design two subsamples from all glasses within a particular RI group were analysed on one day and the remaining two from each glass were analysed on another day. This prevented biasing of inferences, drawn from analysis of the data set, due to random day-to-day fluctuations.

2.2.4 Irradiation and Counting

The irradiation and counting operations were performed at the SLOWPOKE-2 reactor facility situated on the University of Alberta campus.

Irradiation involved exposing the subsamples to a nominal neutron flux of $1X10^{12}$ n cm^{-2} s^{-1} in site #1 of the reactor. The irradiation, delay and counting periods employed were respectively 4, 1 and 5 minutes for the 1-mg samples and 10, 1 and 10 minutes for the 100-μg fragments. In each case the counting period refers to live time. Timing of the irradiation was performed by a digital LED counter which was part of the SLOWPOKE-2 irradiation controller supplied by AECL commercial products. The delay time was obtained via a stopwatch and the counting times (clock time and live time) were obtained by employing a quartz crystal located within the MCA. Prior to positioning of the sample before the detector, the micro-centrifuge tubes were shaken to ensure that the sample was located at the bottom of the tube. Sample placement was at a distance of 1 cm from the detector in a cave which had 10-cm thick lead walls. The height of the cave was 39 cm while the width and length were both 30 cm (internal dimensions). A plastic collar which fit around the detector had a plastic sample rack attached to it. Slots in the rack allowed for precise positioning of the sample card so that the card was held parallel to the endcap of the detector. The plastic sample card contained concentric polyethylene rings which fit snugly around the sample tube. The bottom of the sample tube was aligned to coincide with the centre of the detector crystal.

All counting was carried out with a Model 20180 EG&G ORTEC (Oak Ridge, Tennessee, U.S.A.) horizontal, closed end, hyper-pure (p-type) germanium, coaxial detector system operating at a bias supply of +3500 volts. In addition, a Nuclear Data (ND)-660 multichannel analyser along with an EG&G ORTEC 572 amplifier (coarse gain of 20 and a shaping time of 3 μs) and an ND-575 ADC (4k conversion gain) were coupled to this unit. An EG&G ORTEC 419 precision pulse generator module (operated at 75 Hz) with a

minimum rise time and an attenuation factor of 2 was also included. The detector specifications included a relative efficiency of 22.4% (compared with the efficiency of a 7.5-cm diameter by 7.5-cm thick NaI(Tl) scintillation detector at 25.0 cm), a measured full width half maximum of 1.71 keV and peak-to-Compton ratio of 59.3 : 1 for the 1332 keV photopeak of ^{60}Co. The full width tenth maximum to full width half maximum ratio (FWTM/FWHM) and the full width fiftieth maximum to full width half maximum ratio (FWFM/FWHM) were 1.84 and 2.43 respectively. These ratios reflect the quality of the peak shape, since a Gaussian curve possesses a FWTM/FWHM ratio of 1.82 and a FWFM/FWHM ratio of 2.38. All detector specifications are quoted for a 6-μs amplifier time constant. A mixed radionuclide standardised solution (QCY-44, Amersham Corporation, Amersham, England) emitting a series of 11 principal γ-rays, well spaced in energy from 88 keV to 1.836 MeV, was used for calibration of the system. A two-point calibration was performed using the ^{109}Cd photopeak at 88.037 keV and the ^{60}Co sum peak at 2505.672 keV. The measured radioisotopes with their associated γ-ray energies - ^{24}Na (1369 and 2754 keV), ^{28}Al (1779 keV) and ^{49}Ca (3083 keV) - have half-lives of 14.96 hours, 2.24 minutes and 8.72 minutes respectively. These signals were collected using a 4096 channel spectrum and were stored on floppy disks for later retrieval and analysis.

2.2.5 Spectral Correction and Analysis

Spectral peak searching was accomplished using a software program (PREP 10) supplied by Nuclear Data. The program was integrated into an ND-660 MCA system. Deadtimes of less than 10% were maintained for each subsample. Deadtime corrections[66,67] for the decay of short-lived

radioisotopes in the presence of active, longer-lived isotopes such as ^{24}Na and ^{38}Cl along with a correction factor for random summing effects[68] (pulse pile-up), were calculated using an Apple Macintosh Plus computer with Microsoft Excel software and applied to the photopeaks. The data were also normalised to either correspond to 1 mg or 100 μg of material. The resulting data, with a sample size of 4 for each glass, was then analysed using the Statistical Package for the Social Sciences (SPSS-X) on the University of Alberta Amdahl mainframe computer. The program UANOVA was employed.

2.2.6 Homogeneity Investigations

Panes of glass were obtained from Pittsburgh Plate Glass Canada and AFG Glass Incorporated. The six Pittsburgh samples (n_D = 1.5185, see section 2.2.1 for details) were approximately 45 X 62 cm, with each pane being representative of a one or two month interval between production times. Two panes were nominally 2 mm in thickness, an additional two panes were nominally 3 mm, one was 5 mm, and the last was 6 mm thick. The four AFG panes (n_D = 1.5168, see section 2.2.1 for details) were approximately 38.5 X 61 cm with nominal thicknesses of 2 and 4 mm for each of 2 panes. A 29-day interval existed between production times for samples of the same thickness.

The four corners of each pane were removed using a tungsten carbide wheel cutter (Red Devil 1063) and stored separately. Sample pretreatment and subsample preparation were performed as outlined in sections 2.2.1 and 2.2.2. Only one subsample, however, was removed from each corner at the two increment levels (1-mg and 100-μg). Irradiation and counting, along with spectral correction of the various subsamples, also followed the above described experimental procedures (sections 2.2.3 and 2.2.4).

2.3.1 Detection of Float Glass Samples

The glass samples provided by the RCMP were characterised according to refractive index and type but were not classified according to production mode. This was unfortunate since the difficulty associated with distinguishing between float glass samples has been well documented[36,44] and would provide a rigorous test of any proposed analytical method.

Observation of the glass samples under shortwave UV irradiation was performed because tin contact surfaces have been reported to exhibit a yellowish fluorescence[38] due to the presence of tin oxide. Glass B3 could not be studied in this manner since it was already crushed into small fragments. Several of the glasses demonstrated a strong yellowish fluorescence (A1, A2, A3, B2, B4, D2, D4, E2, E3 and E4). This was taken as evidence of float glass production. The panes of glass known to be manufactured by the float glass process also exhibited this strong fluorescence. In contrast, the fluorescence displayed by the rest of the glasses was much less intense and so their method of production could not be given conclusively. In particular, glass B1 (known to be from a tumbler and hence not produced by the float process) exhibited a slight yellowish colouration when exposed to shortwave UV irradiation. This was further confirmed by the observation of a slight yellowish colouration when a glass vial and a Pasteur pipet were observed under similar illumination.

2.3.2 General Characterisation of the Data Set

Characterisation of the data set was performed using several criteria and some of these criteria were used to justify assumptions required for the statistical analysis that followed. Application of the Kolmogorov-Smirnov one-sample test to the four subsamples of a given glass, after the three repeated measurements on each subsample were averaged, provided no evidence of a non-Gaussian distribution for any of the glasses contained in this study. Assessment of the measurement uncertainty was performed by calculating the %RSD values for the repeated measurements within a particular increment level. Upon averaging the 76 values obtained from the various subsamples at the 1-mg increment level, the overall average measurement uncertainty was 1.6% (1369-keV photopeak, average value range = 0.9_{E4} to $2.3\%_{C2}$) and 1.5% (2754-keV photopeak, average value range = 0.7_{D3} to $2.4\%_{B3}$) for sodium, 2.1% (average value range = 1.0_{A3} to $4.7\%_{E2}$) for aluminum and 4.8% (average value range = 2.4_{B2} to $7.4\%_{E1}$) for calcium. At the 100-μg increment level, these values increased to 2.1% (Na, 1369-keV photopeak, average value range = 1.3_{B4} to $4.5\%_{A1}$), 2.5% (Na, 2754-keV photopeak, average value range = 1.3_{B4} to $3.7\%_{C3}$), 2.4% (Al, average value range = 1.2_{D4} to $4.0\%_{B4}$) and 8.0% (Ca, average value range = 5.7_{D4} to $12.0\%_{A2}$). Since INAA is a non-destructive technique, the determination of the measurement uncertainty did not include an estimate of the uncertainty associated with the weighing process. Ten repeated weighings of the same sample, taken within the space of an hour, resulted in a weighing uncertainty of 1.7 μg. No additional variability was noted when 10 measurements, one measurement per day covering an 11 day period, were obtained on a particular sample. Characterisation of the data set was also obtained using

Currie's criterion[69] for the quantitative determination limit (L_Q). Currie has defined this limit as the minimum number of counts from a radioactive source which will hold the relative statistical uncertainty (%RSD) associated with an analysis to a level of 10%. In this case all of the sodium and aluminum values at both the 1-mg and 100-μg increment levels were found to exceed this limit. However, while this was equally true for the calcium values at the 1-mg level, approximately 12% of the calcium measurements at the 100-μg increment level were found below the L_Q value. These calcium values were equally distributed among the 5 refractive index groups and were found, on average, to be 19 counts below the average L_Q value of 183 counts. Further characterisation was obtained by calculation of Pearson product-moment correlation coefficients. These coefficients were obtained using the following formula

$$r = \Sigma ((X_i - X_{ave})(Y_i - Y_{ave})) / (\Sigma(X_i - X_{ave})^2 \Sigma(Y_i - Y_{ave})^2)^{1/2}$$

$$= r_{A,B} \qquad 2.15$$

where A and B represent the two elements being compared and Σ represents the summation from i=1 to n. Goode and co-workers[47,48] obtained in their NAA investigation the following correlation coefficient values for the three elements being studied here $r_{Na, Al} = -0.29$, $r_{Na, Ca} = -0.34$ and $r_{Al, Ca} = -0.21$. As a result of these calculations, they treated their data as being uncorrelated since they considered that this approximation would not strongly affect the statistical calculations. However, as shown in Tables 2.3.1 and 2.3.2 this was not strictly the case with the data set studied in this investigation. Many strong correlations, with probabilities less than 0.01, are noted and these need to be considered in any statistical calculations used for discrimination of the

Correlation Coefficient	Refractive Index Groups A	B	C	D	E
$r_{Na\text{-}1,\ Na\text{-}2}$	0.7943	0.7468	0.8169	0.8365	0.9496
Probability	0.000	0.000	0.000	0.000	0.000
$r_{Na\text{-}1,\ Al}$	0.3162	- 0.5856	- 0.3876	- 0.4479	0.8457
Probability	0.014	0.000	0.010	0.001	0.000
$r_{Na\text{-}1,\ Ca}$	0.3213	- 0.3193	0.4637	0.0503	- 0.1169
Probability	0.013	0.013	0.002	0.367	0.214
$r_{Na\text{-}2,\ Al}$	0.4196	- 0.6484	- 0.3468	- 0.4643	0.8442
Probability	0.001	0.000	0.019	0.000	0.000
$r_{Na\text{-}2,\ Ca}$	0.2467	- 0.3473	0.3617	0.0427	- 0.1342
Probability	0.046	0.008	0.015	0.387	0.182
$r_{Al,\ Ca}$	- 0.1259	0.7185	0.1538	0.2201	- 0.0719
Probability	0.197	0.000	0.185	0.066	0.314

Table 2.3.1 Pearson Product-Moment Correlation Coefficients and Probability Values For Elements Found in 100–µg Subsamples of Glass Covering Five Refractive Index Groups.

Correlation Coefficient	Refractive Index Groups A	B	C	D	E
$r_{Na\text{-}1,\ Na\text{-}2}$	0.7828	0.8342	0.8770	0.9420	0.9632
Probability	0.000	0.000	0.000	0.000	0.000
$r_{Na\text{-}1,\ Al}$	0.4430	- 0.5855	- 0.6940	- 0.6003	0.9352
Probability	0.001	0.000	0.000	0.000	0.000
$r_{Na\text{-}1,\ Ca}$	- 0.0793	- 0.4341	0.0668	- 0.1911	- 0.3532
Probability	0.296	0.001	0.349	0.097	0.007
$r_{Na\text{-}2,\ Al}$	0.4016	- 0.6312	- 0.7964	- 0.6433	0.9254
Probability	0.002	0.000	0.000	0.000	0.000
$r_{Na\text{-}2,\ Ca}$	- 0.0638	- 0.5122	0.0900	- 0.2004	- 0.3367
Probability	0.333	0.000	0.301	0.086	0.010
$r_{Al,\ Ca}$	- 0.4498	0.9338	0.0384	0.1846	- 0.3107
Probability	0.001	0.000	0.412	0.104	0.016

Table 2.3.2 Pearson Product-Moment Correlation Coefficients and Probability Values For Elements Found in 1-mg Subsamples of Glass Covering Five Refractive Index Groups.

various glasses. Specifically, a variance-covariance matrix must be considered in any multi-elemental approach employed in the analysis of this data.

2.3.3 The Overall Statistical Model

In statistics, although not always explicitly stated, the notion of a model is a central concept which makes hypothesis testing feasible. In each of the statistical tests presented thus far, the assumption of the data being generated from some ideal distribution may be considered as modelling. In general, a statistical model consists of a body of assumptions, mathematical in nature with a random component, that describe the experimenter's understanding of the physical basis underlying the experiment. At this stage, careful consideration of the possible sources of variation contained within any experiment is extremely important. This importance may be easily understood by expressing the F-value as the ratio of the explained to unexplained variance, i.e.

$$F = \text{explained variance} / \text{unexplained variance} \qquad 2.16$$

As the variance in an experiment is more completely explained by the various systematic terms in the model, the value of the numerator is increased while at the same time the denominator decreases. Thus, the ability to detect whether one term is important is strengthened by a more complete accounting of the explained variance within any experiment. This more thorough consideration of the variance permits a more sensitive test of any proposed hypothesis.

The overall statistical model for the nineteen glasses in this investigation may be represented as a linear combination of several population treatment effects

$$Y = \eta + Glass + Size + Size * Glass + Subsample + Size * Subsample + Repeat + Size * Repeat + Error \qquad 2.17$$

where Y is a response function or matrix consisting of the levels of the elements Na, Al and Ca found in a particular glass. The Grand Mean, η, along with the treatment and interaction effects are also column vectors. The Grand Mean may be considered an origin from which all deviations are measured and the effects may be viewed as representing these deviations. The final term in equation 2.17, the random Error term, is the cumulative effect of other variables that may be unknown to the experimenter or are very small in magnitude and as such do not appear as separate identifiable entities in the model. The Glass, Size, Subsample and Repeat effects all account for the possibility that different levels of these various terms may result, on average, in different responses being observed. For example, the choice of a particular glass within a certain RI group will dictate the amount of sodium, aluminum and calcium detected. Likewise, depending on the size of the subsample increment chosen, different responses may be observed due to homogeneity considerations. These isolated effects are termed main effects. This is in direct contrast to the Size * Glass interaction effect listed in equation 2.17. This term accounts for any nonadditivity of the Size and Glass responses. It implies that the two responses act in conjunction with one another to give a slightly modified response that cannot be accounted for by the main effects alone. This response may be of a synergistic or interfering nature. Further

classification of the effects in the model may be performed according to whether their choice is a random or fixed event. In this case, the Size and Glass effects are considered fixed effects since only distinct levels are tested while the particular subsample chosen and the repeated measurements are considered as being taken randomly from a particular distribution. Finally, the Error term may be viewed as an aggregate of a number of component errors

$$\varepsilon = a_1 \varepsilon_1 + a_2 \varepsilon_2 + a_3 \varepsilon_3 + \ldots + a_n \varepsilon_n \qquad 2.18$$

where the a's represent constants. According to the central limit theorem, the distribution of such a linear function of errors will tend to normality (under certain conditions) as the number of components becomes large, almost irrespective of the individual distributions of the components. This will occur when the ε's are uncorrelated, when several of the sources of error make important contributions to the overall error and, in particular, when no single source of error dominates all the rest. These conditions are usually met in the real world of experimentation. Modelling is an important endeavour because the establishment of a relationship between the terms in a model and the response function, Y, will enable the effect on Y of changing certain experimental parameters to be forecast in advance. Modelling is also important since it permits testing of the individual terms comprising a model. This may lead to further insight and even a more thorough understanding of the physical basis underlying an experiment.

2.3.4 Statistical Data Analysis

Analysis of the glass data was performed using the King-Henderson algorithm[70] as the mean square model. Testing of the main effects along with the interaction terms by means of an F-test provided further insight into whether the various factors were making statistically discernible contributions to the observations. The various model equations appear in Figure 2.3.1. Results of the variance analysis for the five refractive index groups are presented in Tables 2.3.3 to 2.3.10. In each case, the Grand Mean and Size terms have been excluded since each one showed very strong evidence (i.e. a probability of approximately zero) for a statistically discernible difference in both the multivariate and univariate cases. This result is not surprising for the Grand Mean and simply indicates its nonzero value. Interpretation of the Size term is difficult, however, since there is a confounding of effects. This indicates that the amount of sodium, for example, found in a 1-mg subsample is not the same as that found for a 100-μg fragment. As the sample size gets smaller, the heterogeneous distribution of sodium in the sample may account for the noted difference or the difference may simply be due to the experimental conditions under which each sample was analysed. The latter hypothesis recognizes that differences may arise because the two sample increment sizes were irradiated and counted for different time periods. Note that even though the number of counts contained in a photopeak may not be due entirely to one element owing to interfering reactions (e.g. $^{28}Si(n, p)^{28}Al$, $^{24}Mg(n, p)^{24}Na$ and $^{27}Al(n, \alpha)^{24}Na$) comparisons among glasses would not be affected. This is because the composite photopeaks and the information contained in them are still unique for a particular glass. Further investigation of the Size effect was felt to

Model 1:	Grand Mean
Model 2:	Size
Equation	Error + Size*Repeat (Subsample, Glass) + 3*Size*Subsample (Glass) + Size
Model 3:	Glass
Equation	Error + Size*Repeat (Subsample, Glass) + 2*Repeat (Subsample, Glass) + 3*Size*Subsample (Glass) + 6*Subsample (Glass) + Glass
Model 4:	Size*Glass
Equation	Error + Size*Repeat (Subsample, Glass) + 3*Size*Subsample (Glass) + Size*Glass
Model 5:	Subsample (Glass)
Equation	Error + Size*Repeat (Subsample, Glass) + 2*Repeat (Subsample, Glass) + 3*Size*Subsample (Glass) + 6*Subsample (Glass)
Model 6:	Size*Subsample (Glass)
Equation	Error + Size*Repeat (Subsample, Glass) + 3*Size*Subsample (Glass)
Model 7:	Repeat (Subsample, Glass)
Equation	Error + Size*Repeat (Subsample, Glass) + 2*Repeat (Subsample, Glass)
Model 8:	Size*Repeat (Subsample, Glass)
Equation	Error + Size*Repeat (Subsample, Glass)

Figure 2.3.1 Terms of the Overall Statistical Model and Their Variance Components.

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	3.804	12.000	33.000	0.001
Hotellings Trace	243.89	12.00	23.00	0.00
Wilk's Lambda	27.7644	12.0000	24.1033	0.0000

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	5.51	3	12	0.0130
Na-2	6.13	3	12	0.0091
Al	901.10	3	12	0.0000
Ca	13.85	3	12	0.0003

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	0.743	48.000	128.000	0.879
Hotellings Trace	0.76	48.00	110.00	0.86
Wilk's Lambda	0.7512	48.0000	113.7497	0.8674

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	0.81	12	32	0.6350
Na-2	1.45	12	32	0.1956
Al	0.57	12	32	0.8474
Ca	0.48	12	32	0.9091

Table 2.3.3 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Glass and Subsample Terms of the Overall Statistical Model (A Group, $n_D = 1.5171$).

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size*Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.349	128.000	128.000	0.046
Hotellings Trace	1.26	128.00	110.00	0.11
Wilk's Lambda	1.3051	128.0000	118.0082	0.0714

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	2.05	32	32	0.0235
Na-2	1.36	32	32	0.1965
Al	1.05	32	32	0.4428
Ca	1.47	32	32	0.1413

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	4.370	12.000	33.000	0.000
Hotellings Trace	8948.19	12.00	23.00	0.00
Wilk's Lambda	118.3182	12.0000	24.1033	0.0000

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	35.41	3	12	0.0000
Na-2	25.62	3	12	0.0000
Al	20743.23	3	12	0.0000
Ca	81.50	3	12	0.0000

Table 2.3.4 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Repeat (A Group, n_D = 1.5171) and Glass (B Group, n_D = 1.5185) Terms of the Overall Statistical Model.

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.046	48.000	128.000	0.411
Hotellings Trace	1.09	48.00	110.00	0.35
Wilk's Lambda	1.0714	48.0000	113.7497	0.3758

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	0.56	12	32	0.8536
Na-2	1.26	12	32	0.2863
Al	0.79	12	32	0.6586
Ca	1.29	12	32	0.2742

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size*Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.217	128.000	128.000	0.133
Hotellings Trace	1.18	128.00	110.00	0.19
Wilk's Lambda	1.2012	128.0000	118.0082	0.1565

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	1.33	32	32	0.2142
Na-2	0.74	32	32	0.8046
Al	1.02	32	32	0.4815
Ca	1.39	32	32	0.1790

Table 2.3.5 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Subsample and Repeat Terms of the Overall Statistical Model (B Group, $n_D = 1.5185$).

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.954	8.000	14.000	0.130
Hotellings Trace	360.61	8.00	10.00	0.00
Wilk's Lambda	35.6324	8.0000	12.0000	0.0000

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	75.13	2	9	0.0000
Na-2	113.17	2	9	0.0000
Al	413.50	2	9	0.0000
Ca	0.14	2	9	0.8735

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	0.681	36.000	96.000	0.903
Hotellings Trace	0.60	36.00	78.00	0.96
Wilk's Lambda	0.6384	36.0000	80.4340	0.9319

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	0.89	9	24	0.5491
Na-2	0.80	9	24	0.6221
Al	0.47	9	24	0.8788
Ca	0.51	9	24	0.8515

Table 2.3.6 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Glass and Subsample Terms of the Overall Statistical Model (C Group, $n_D = 1.5157$).

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size*Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.106	96.000	96.000	0.311
Hotellings Trace	1.01	96.00	78.00	0.49
Wilk's Lambda	1.0612	96.0000	85.7097	0.3906

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	1.16	24	24	0.3618
Na-2	0.82	24	24	0.6853
Al	1.49	24	24	0.1688
Ca	1.89	24	24	0.0626

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	6.815	12.000	33.000	0.000
Hotellings Trace	179.63	12.00	23.00	0.00
Wilk's Lambda	60.5664	12.0000	24.1033	0.0000

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	74.75	3	12	0.0000
Na-2	99.35	3	12	0.0000
Al	446.58	3	12	0.0000
Ca	1.30	3	12	0.3202

Table 2.3.7 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Repeat (C Group, n_D = 1.5157) and Glass (D Group, n_D = 1.5168) Terms of the Overall Statistical Model.

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.285	48.000	128.000	0.136
Hotellings Trace	1.44	48.00	110.00	0.06
Wilk's Lambda	1.3772	48.0000	113.7497	0.0853

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	2.48	12	32	0.0202
Na-2	1.06	12	32	0.4247
Al	2.81	12	32	0.0096
Ca	1.04	12	32	0.4352

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size*Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.356	128.000	128.000	0.043
Hotellings Trace	1.40	128.00	110.00	0.04
Wilk's Lambda	1.3792	128.0000	118.0082	0.0386

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	0.90	32	32	0.6154
Na-2	1.96	32	32	0.0303
Al	0.99	32	32	0.5149
Ca	1.79	32	32	0.0529

Table 2.3.8 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Subsample and Repeat Terms of the Overall Statistical Model (D Group, $n_D = 1.5168$).

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	5.083	12.000	33.000	0.000
Hotellings Trace	475.66	12.00	23.00	0.00
Wilk's Lambda	50.7171	12.0000	24.1033	0.0000

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	239.32	3	12	0.0000
Na-2	175.07	3	12	0.0000
Al	2852.26	3	12	0.0000
Ca	6.41	3	12	0.0077

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.044	48.000	128.000	0.415
Hotellings Trace	1.05	48.00	110.00	0.41
Wilk's Lambda	1.0500	48.0000	113.7497	0.4078

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	1.22	12	32	0.3096
Na-2	1.09	12	32	0.3973
Al	0.88	12	32	0.5761
Ca	0.50	12	32	0.9007

Table 2.3.9 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Glass and Subsample Terms of the Overall Statistical Model (E Group, $n_D = 1.5191$).

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size*Repeat (Subsample, Glass)

Multivariate F-Ratios

Test	F-Ratio	DFH	DFE	Probability
Pillais Criterion	1.095	128.000	128.000	0.305
Hotellings Trace	1.22	128.00	110.00	0.14
Wilk's Lambda	1.1578	128.0000	118.0082	0.2100

Univariate F-Ratios

Variable	F-Ratio	DF1	DF2	Probability
Na-1	1.28	32	32	0.2455
Na-2	1.62	32	32	0.0884
Al	1.25	32	32	0.2688
Ca	1.22	32	32	0.2894

Table 2.3.10 Multivariate and Univariate F-Ratios, Degrees of Freedom and Probability Values For the Repeat Term of the Overall Statistical Model (E Group, n_D = 1.5191).

be unwarranted from a practical standpoint because comparable increment sizes would usually be employed in any investigation. Interpretation of the interaction terms was not pursued for the same reason.

To test the remaining terms of the model a multivariate and univariate F-test analysis was performed. In the multivariate case, the data were tested for any statistically discernible differences between population mean vectors for glasses found within a particular refractive index group. Several multivariate procedures were performed since there is no simple, clear cut answer as to which procedure should be used. Each procedure is particularly sensitive to certain variations exhibited by the data set of interest. In examining the Glass term, refractive index groups A, B, D and E were noted to exhibit strong evidence of inhomogeneity. This implies that at least one glass in each of these RI groups possesses a mean vector which is statistically discernible from those of the other glasses in the group. In group C, Pillai's criterion[71,72] indicated a probability value of 0.130 while both Hotelling's Trace[71,72] and Wilk's Lambda[71,72] gave a probability value of approximately zero. This discrepancy resulted because Pillai's criterion is particularly sensitive to any variations which occur predominantly in one dimension. It appears that the deviation resulted in this particular case from the wide range of results obtained for aluminum. To investigate the multivariate response further, it is necessary to recall that there was considerable correlation between the various elements. Calculation of the univariate F-ratios is of particular interest here because they aid in determining whether these differences in mean vectors are attributable to influences from all four variables, or whether certain variables contribute to these differences because of their correlation with, for example, aluminum. In

this circumstance, sodium (both Na-1, the photopeak at 1369 keV and Na-2, the photopeak at 2754 keV) and aluminum contributed in making the mean vector of at least one glass statistically discernible from the rest. Similar analysis of groups A, B, D and E revealed Al and Ca to be important contributors, along with Na-2 to a lesser extent, to the differences noted between glasses in group A. In group B, all the variables and Na-1, Na-2 and Al in groups D and E are the relevant variables which made important contributions to the noted differences in the mean vectors. Calcium also contributed to the observed differences noted in group E.

In groups A, B and C (Tables 2.3.3 to 2.3.7) there is no evidence by either the multivariate or univariate procedures to suggest the existence of a statistically discernible difference in the population means for any of the elements when the Subsample and Repeat terms were considered. Specifically, this indicates that these terms do not aid in distinguishing between the various glasses found within these refractive index sets. In contrast to this, group D exhibited an aluminum univariate F-value with a probability of 0.0096 (Table 2.3.8) for the Subsample term. This suggested that not all of the subsamples from a particular glass could be viewed as being indistinguishable from one another. However, since the probability value was very close to the 1% significance level, further study of the glasses in group D (i.e. more data) would be warranted to definitely determine whether the aluminum values for certain subsamples were actually discernible from other subsamples taken from the same glass. If a statistically discernible difference was obtained, it would be best to take a number of subsamples when glasses within this group were analysed, in order to prevent any biasing of the inferences due to sampling error. The remaining terms for both groups

D and E showed no statistically discernible differences. In general, the nineteen glasses exhibited "local" homogeneity, where "local" acknowledges that the subsamples were taken from fragments of glass which typically had small dimensions. Additionally, the Repeat term indicated that the variability associated with the measurement technique did not discernibly aid in the discrimination of glasses found within the same RI group.

The conclusion, from a statistically discernible univariate F-ratio result, is that at least one of the glasses in a data set is distinguishable (in the sense of a difference in mean response) from the others based on the particular element considered. To determine which specific glasses are distinguishable from the others it is necessary to look at procedures called multiple comparisons tests. In this case, the multiple comparisons test used was Tukey's alternate procedure (Tukey B). The hypothesis term for the comparisons was Size * Glass and an experimentwise error rate of 0.01 was employed. Since the model equation for the Tukey B procedure was Size * Glass, this represented a fixed effects model. Coupling of this fixed effects model with a balanced design (i.e. equal sample sizes) meant that the statistical tests in this section were reasonably insensitive to deviations from the homogeneity of variance assumption[73]. This is important because analyses where both of these conditions do not apply must account for the possibility of heterogeneous variances whenever a pooling of the variances takes place. Failure to test for this heterogeneity of variance may result in a situation where the type I error is dramatically increased beyond the level to which an experimenter believes it is controlled.

The results of these multiple comparisons appear in Tables 2.3.11 to 2.3.15. The quoted probabilities are for the LSDD procedure (pairwise error

	Probability Values			
	1-mg Subsamples		100-µg Subsamples	
Na-1 Comparison	Tukey B	t-test	Tukey B	t-test
A1 vs. A2	NSD	NSD	NSD	NSD
A1 vs. A3	NSD	NSD	NSD	NSD
A1 vs. A5	*	++	NSD	NSD
A2 vs. A3	NSD	NSD	NSD	NSD
A2 vs. A5	*	NSD	NSD	NSD
A3 vs. A5	*	++	NSD	NSD
Na-2 Comparison				
A1 vs. A2	NSD	NSD	NSD	NSD
A1 vs. A3	NSD	NSD	NSD	NSD
A1 vs. A5	**	+	NSD	NSD
A2 vs. A3	NSD	NSD	NSD	NSD
A2 vs. A5	*	NSD	NSD	NSD
A3 vs. A5	**	++	NSD	NSD
Al Comparison				
A1 vs. A2	***	++	***	++
A1 vs. A3	***	++	NSD	NSD
A1 vs. A5	***	++	*	NSD
A2 vs. A3	***	++	***	++
A2 vs. A5	***	++	***	++
A3 vs. A5	***	++	***	+
Ca Comparison				
A1 vs. A2	NSD	NSD	NSD	NSD
A1 vs. A3	NSD	NSD	NSD	NSD
A1 vs. A5	**	NSD	NSD	NSD
A2 vs. A3	NSD	NSD	NSD	NSD
A2 vs. A5	***	++	NSD	NSD
A3 vs. A5	***	+	NSD	NSD

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001
* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 2.3.11 Tukey B and t-test Probability Values For Pairwise Comparisons of the A Glasses Using Four 1-mg or Four 100-µg Subsamples of Each Glass.

	Probability Values			
	1-mg Subsamples		100-µg Subsamples	
Na-1 Comparison	Tukey B	t-test	Tukey B	t-test
B1 vs. B2	***	++	**	+
B1 vs. B3	**	+	*	NSD
B1 vs. B4	***	+	NSD	NSD
B2 vs. B3	***	++	NSD	NSD
B2 vs. B4	**	++	NSD	NSD
B3 vs. B4	NSD	NSD	NSD	NSD
Na-2 Comparison				
B1 vs. B2	***	++	**	++
B1 vs. B3	***	NSD	**	++
B1 vs. B4	***	+	*	NSD
B2 vs. B3	**	+	NSD	NSD
B2 vs. B4	*	+	NSD	NSD
B3 vs. B4	NSD	NSD	NSD	NSD
Al Comparison				
B1 vs. B2	***	++	***	++
B1 vs. B3	***	++	***	++
B1 vs. B4	***	++	***	++
B2 vs. B3	*	NSD	NSD	NSD
B2 vs. B4	NSD	NSD	NSD	NSD
B3 vs. B4	**	+	NSD	NSD
Ca Comparison				
B1 vs. B2	***	++	**	+
B1 vs. B3	***	++	**	+
B1 vs. B4	***	++	**	+
B2 vs. B3	NSD	NSD	NSD	NSD
B2 vs. B4	NSD	NSD	NSD	NSD
B3 vs. B4	NSD	NSD	NSD	NSD

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001

* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 2.3.12 Tukey B and t-test Probability Values For Pairwise Comparisons of the B Glasses Using Four 1-mg or Four 100-µg Subsamples of Each Glass.

	Probability Values			
	1-mg Subsamples		100-µg Subsamples	
Na-1 Comparison	Tukey B	t-test	Tukey B	t-test
C1 vs. C2	NSD	NSD	NSD	NSD
C1 vs. C3	***	++	*	NSD
C2 vs. C3	***	++	**	++
Na-2 Comparison				
C1 vs. C2	NSD	NSD	NSD	NSD
C1 vs. C3	***	++	*	NSD
C2 vs. C3	***	++	**	++
Al Comparison				
C1 vs. C2	NSD	NSD	NSD	NSD
C1 vs. C3	***	++	***	+
C2 vs. C3	***	++	**	++
Ca Comparison				
C1 vs. C2	NSD	NSD	NSD	NSD
C1 vs. C3	NSD	NSD	NSD	NSD
C2 vs. C3	NSD	NSD	NSD	NSD

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001
* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 2.3.13 Tukey B and t-test Probability Values For Pairwise Comparisons of the C Glasses Using Four 1-mg or Four 100-µg Subsamples of Each Glass.

	Probability Values			
	1-mg Subsamples		100-µg Subsamples	
Na-1 Comparison	Tukey B	t-test	Tukey B	t-test
D1 vs. D2	***	++	**	NSD
D1 vs. D3	***	++	***	++
D1 vs. D4	***	++	***	+
D2 vs. D3	NSD	+	NSD	NSD
D2 vs. D4	NSD	NSD	NSD	NSD
D3 vs. D4	**	+	NSD	NSD
Na-2 Comparison				
D1 vs. D2	***	++	***	NSD
D1 vs. D3	***	++	***	+
D1 vs. D4	***	++	*	NSD
D2 vs. D3	*	NSD	NSD	NSD
D2 vs. D4	NSD	NSD	NSD	NSD
D3 vs. D4	***	++	NSD	+
Al Comparison				
D1 vs. D2	***	+	NSD	NSD
D1 vs. D3	***	++	***	++
D1 vs. D4	***	++	NSD	NSD
D2 vs. D3	***	++	***	++
D2 vs. D4	NSD	NSD	NSD	NSD
D3 vs. D4	***	++	***	++
Ca Comparison				
D1 vs. D2	NSD	NSD	NSD	NSD
D1 vs. D3	NSD	NSD	NSD	NSD
D1 vs. D4	NSD	NSD	NSD	NSD
D2 vs. D3	NSD	NSD	NSD	NSD
D2 vs. D4	NSD	NSD	NSD	NSD
D3 vs. D4	NSD	NSD	NSD	NSD

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001
* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 2.3.14 Tukey B and t-test Probability Values For Pairwise Comparisons of the D Glasses Using Four 1-mg or Four 100-µg Subsamples of Each Glass.

	Probability Values			
	1-mg Subsamples		100-µg Subsamples	
Na-1 Comparison	Tukey B	t-test	Tukey B	t-test
E1 vs. E2	***	++	***	++
E1 vs. E3	***	++	***	++
E1 vs. E4	***	++	***	+
E2 vs. E3	NSD	NSD	NSD	NSD
E2 vs. E4	NSD	NSD	NSD	NSD
E3 vs. E4	NSD	NSD	NSD	NSD
Na-2 Comparison				
E1 vs. E2	***	++	***	++
E1 vs. E3	***	++	***	++
E1 vs. E4	***	++	***	+
E2 vs. E3	NSD	NSD	NSD	NSD
E2 vs. E4	NSD	NSD	NSD	NSD
E3 vs. E4	NSD	NSD	NSD	NSD
Al Comparison				
E1 vs. E2	***	++	***	++
E1 vs. E3	***	++	***	++
E1 vs. E4	***	++	***	++
E2 vs. E3	***	++	***	+
E2 vs. E4	***	++	***	++
E3 vs. E4	***	++	NSD	NSD
Ca Comparison				
E1 vs. E2	*	NSD	NSD	NSD
E1 vs. E3	NSD	NSD	NSD	NSD
E1 vs. E4	**	NSD	NSD	NSD
E2 vs. E3	NSD	NSD	NSD	NSD
E2 vs. E4	NSD	NSD	NSD	NSD
E3 vs. E4	NSD	NSD	NSD	NSD

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001
* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 2.3.15 Tukey B and t-test Probability Values For Pairwise Comparisons of the E Glasses Using Four 1-mg or Four 100-µg Subsamples of Each Glass.

rate) and constitute a limitation of the program UANOVA. Since the LSDD procedure employs a pairwise error rate, while the Tukey B method employs an experimentwise error rate, the LSDD procedure should, on average, indicate more statistically discernible differences. This, however, was not the case and a direct correspondence, in the sense that the two procedures agreed on what was statistically discernible, was noted. Thus, although the quoted probability values cannot be considered to be absolutely correct, they should provide an excellent approximation of this quantity.

In general, the results of the multiple comparisons analysis of three repeat measurements on each of four subsamples for each glass in a certain refractive index group is very encouraging. Overall, at the 1-mg increment level 90% of all the pairwise comparisons between glasses of the same RI are able to be distinguished when a 1% experimentwise error rate is employed. Distinguished is used, here, in the sense that two glasses are deemed distinguishable when a pairwise comparison results in a probability value of 0.01 or less for at least one of the elements. At the 100-μg level, 73% of all the pairwise comparisons are distinguishable. The differences are generally quite marked, with probability values of less than 1 in 10,000 being common. Aluminum was found to be the best discriminating element, followed by sodium and then calcium. Also appearing in Tables 2.3.11 to 2.3.15 are the results of a classical t-test of the difference between two means using a pooled (weighted average) variance term. These have been included to provide a more complete evaluation of the Tukey multiple comparisons procedure. In general, Tukey's method is more sensitive to deviations in the levels of the elements for the glasses. In this particular case, Tukey's procedure found 5% more statistically discernible differences at the 1-mg increment level, but this

did not translate into any greater discrimination being observed (i.e. both methods showed a 90% discrimination rate). A difference was noted, however, at the 100-µg level. Here Tukey's procedure found 8% more statistically discernible differences, and the pairwise discrimination rate dropped from 73 to 66% when the t-test was employed.

Of the 19 glasses in this study, 18 were classified as flat glass. Only one glass (B1) was obtained from a tumbler and this glass would be classified as tableware. Comparison of glass B1 to the other glasses indicated its Ca and Al values were very distinctive and gave the highest average values for the 19 glasses at both increment levels. These elevated values appear to be in good agreement with levels found in cheaper transparent tableware glass, which has practically the same composition as container glass[74]. Typical values for CaO in container glass range from 9.6 to 11.5% while modern flat glass has approximately 7 to 10% CaO[75,76].

In considering the remaining 18 flat glasses, glasses A1, A2, A3, B2, B4, D2, D4, E2, E3 and E4 were of particular interest because they were believed to have been produced by the float glass process. At the 1-mg increment level (Tables 2.3.11 to 2.3.15), the A glasses were readily distinguished from one another based on their aluminum content, the B glasses were easily discerned based on their sodium values and the E glasses were readily discriminated on the basis of their aluminum values. Only glasses D2 and D4 could not be distinguished on the basis of any of the studied elements. When the results were considered for the 100-µg increment level, glasses A1 and A3 could no longer be distinguished, but glasses A1 and A2 along with A2 and A3 could still be distinguished on the basis of their aluminum values. In addition, glasses B2 and B4 along with D2 and D4 could no longer be discriminated on

the basis of any of the studied elements. This was also true for the comparison of glasses E3 and E4, but differences between glasses E2 and E3, and between E2 and E4, were still discernible.

Two sodium photopeaks were studied throughout the above analyses. It appears from the data in this investigation that no apparent difference exists between the information provided by the two photopeaks despite their location in different parts of the γ-ray spectrum (see Figure 1.4.1) and the considerably different background values associated with each. Therefore, in further studies only one or the other sodium photopeak need be considered. The choice may be made on the basis of spectral interference with one or the other, or on convenience when measuring the spectra.

The above comparisons have all considered the analysis of four subsamples with three repeat determinations per subsample. A more realistic situation would be a case where a significant amount of the control glass (the glass obtained at the scene of a crime) is present but only a limited amount of glass is available from the suspect. To pursue this point further, a t-test of the difference between two means was incorporated into a Lightspeed Pascal computer program on the Macintosh. This program assumed four subsamples at either of the increment levels were available from the control glass sample while only one subsample was obtained from the suspect. It also assumed that one measurement had been performed on each subsample. Another implicit assumption resulting from the use of only one suspect sample was that the variances associated with the suspect and control glass samples were identical. The program then computed all the possible combinations for the control and suspect glasses from the data set which included 3 repeat measurements on each of the four subsamples for each

glass. Thus, there were 81 combinations for each control glass sample and 12 combinations for each suspect sample. The probability values for these 972 combinations were obtained and an average probability value was calculated. The results of this study were that 50% of the pairwise comparisons at the 1-mg increment level resulted in discrimination while only 26% of the comparisons at the 100-μg level resulted in the glasses being distinguishable at the 1% significance level.

Several additional practical considerations should be discussed at this point. Refractive index measurements because they are fast, inexpensive and relatively simple to perform will still continue to be the primary method used for the discrimination of glass samples. However, when these analyses are not conclusive it may be necessary to employ a complementary technique such as INAA. It is suggested that all of the available glass fragments found to be indistinguishable by RI measurements should be analysed separately at first by INAA. This recognises the fact that many glasses having the same RI values may possess widely variant chemical compositions. The fragments that are indistinguishable by INAA may then be identified. Further discrimination may result by crushing single fragments, if sufficient material is available, to produce several smaller test portions. Subsequent analysis of the smaller fragments can be performed and the elemental distribution noted. Pooling of the original fragments found to be indistinguishable by INAA is not recommended.

2.3.5 Analysis of Float Glass Panes

The results for the investigation of different panes provided by two Canadian flat glass manufacturers may be summarised in the following

manner. For both manufacturers there was no evidence to suggest any deviation from normality when the within-pane results were studied using the Kolmogorov-Smirnov one-sample test. Using Currie's criterion[69], only one calcium value (at the 100-μg increment level) was found to be below the critical limit of determination. For each of the increment levels (1-mg and 100-μg), the various panes produced by a given manufacturer were found to be homogeneous for Na, Al and Ca when within- (using the Studentized Range Test at a 10% significance level) and between- (using ANOVA tables at a 5% significance level) pane comparisons were performed. Since the panes were produced at different times from different batches, this homogeneity also indicated a stable or consistent supply of raw materials, along with reliable control of the production process.

Another point of interest arising from this study is a comparison of the glass formulations of each manufacturer. These results appear in Table 2.3.16. In each case the results reported are an average for all the analyses performed on the glass panes studied. This corresponds to 16 measurements (4 measurements on each of 4 panes) for the AFG-produced glass and 24 (4 measurements on each of 6 panes) for the Pittsburgh glass samples. For both increment levels a statistically discernible difference in the aluminum content of the glasses was noted (i.e. the probability that the two glasses possess the same mean aluminum level is less than 1 in 10,000). Comparison of the two values shows the Al content of the AFG samples to be approximately double that found in the Pittsburgh samples. A statistically discernible difference (i.e. a probability value of 0.003) in the calcium levels for the two manufacturers was also evident for 1-mg sized subsamples. Testing of the average elemental values for each manufacturer was

100-μg Subsamples	Manufacturer	
Elements	AFG	Pittsburgh
Na-1	7347	7480
Na-2	3717	3759
Al	5152	2626
Ca	212	213
1-mg Subsamples		
Na-1	14771	14970
Na-2	7413	7534
Al	29201	12765
Ca	610	644

Table 2.3.16 Flat Glass Formulations For Two Major Canadian Manufacturers. The reported values are the average counts for a total of 16 analyses on 4 AFG-produced panes or 24 analyses on 6 Pittsburgh-produced panes.

performed using a t-test of the difference between two means and employed a weighted average of the variances of the two samples. Determination of the precision of this technique (i.e. analytical uncertainty) was possible since the within- and between-pane comparisons, at both increment levels, for each manufacturer showed no evidence of heterogeneity for sodium, aluminum or calcium. For the sample sets of 16 and 24 fragments, a %RSD (1-mg sample) of 1.2% (Na-1) was obtained for the AFG-produced glass while a value of 2.2% was obtained for the Pittsburgh glass. The Na-2, Al and Ca values for the AFG (Pittsburgh) samples were respectively 1.8 (2.5), 1.7 (3.6) and 4.2 (5.5) %. At the 100-μg increment level these values rose slightly in general, and attained values of 2.1 (2.4), 2.4 (2.6), 3.4 (11.8) and 5.5 (8.8)% for Na-1, Na-2, Al and Ca respectively. An additional point of interest was the comparison of these glass samples, which had a known origin, to the glasses of unknown origin provided by the RCMP. From the analyses performed, it appears that the glass samples of Canadian origin are statistically discernible at the 1-mg increment level from all of the nineteen glasses. Thus, it is unlikely that any of the glass fragments provided by the RCMP were produced by either of the major Canadian flat glass manufacturers studied in this investigation.

Chapter 3

Introduction

3.1.1 The Cyclic Instrumental Neutron Activation Analysis Experiment

In cyclic instrumental neutron activation analysis (CINAA) short half-life nuclides ($t_{1/2}$ < 65 seconds) are preferentially activated by maintaining short irradiation and counting times, on the order of the half-life of the radionuclide of interest. By repeatedly cycling a sample between an irradiating source and detector, enhanced signal-to-noise ratios relative to those of a conventional one-shot INAA analysis scheme are obtained. Under these conditions, the contribution made by longer-lived isotopes to the background signal is considerably reduced.

In CINAA, the total experimental time (T_0) may be considered the sum of v repetitive cycle periods (T). This may be expressed mathematically as

$$T_0 = \Sigma T$$

For the summation from i=1 to v

$$T_0 = vT \qquad 3.1$$

and

$$T = t_i + t_w + t_c + t_{w'} \qquad 3.2$$

where t_i is the time of irradiation, t_w is the duration of time between the end of irradiation and the start of counting, t_c is the counting time, $t_{w'}$ is the

elapsed time between the end of counting and the start of irradiation and each of these time intervals is measured in seconds. These components of the cycle period are illustrated in Figure 3.1.1 where the isotope activity is plotted versus time in a cyclic neutron activation analysis experiment.

This continued enhancement of the signal-to-noise ratio is, however, limited in practice to total experimental times that are approximately twenty times the half-life of the isotope of interest[78]. At this point, the relative advantage in the signal-to-noise ratio, gained by cycling the sample, does not vary appreciably. Figure 3.1.2, where the signal-to-noise (i.e. signal-to-(background)$^{1/2}$) ratio is plotted versus m ($T_0/t_{1/2}$ or the total experimental time per half-life of the isotope of interest) for both the conventional (one-shot) and cyclic analysis techniques, illustrates this point. In this plot the half-life of the predominant isotope in the background underlying the signal is assumed to be 100 times that of the half-life of the isotope of interest. This condition is not an unrealistic situation since in biological/environmental and other matrices isotopes such as ^{77m}Se ($t_{1/2}$ = 17.4 s), ^{20}F ($t_{1/2}$ = 11.2 s) and ^{179m}Hf ($t_{1/2}$ = 18.6 s) may be measured. In the ideal case, where the waiting times are zero (minimal) an enhanced signal-to-noise ratio in favour of the CINAA technique is realised when the total experimental time is approximately 2.5 times the half-life of the isotope of interest. This value increases to approximately 4.5 and 6.0 times when the waiting times are increased from one-third to one-half the half-life. In addition to improved detection limits for γ-rays emitted by short-lived nuclides, CINAA also offers more efficient use of the reactor and counting facilities since results from short and long-lived nuclides of the same element have yielded results in good agreement with one another[80]. Further, the technique has also been

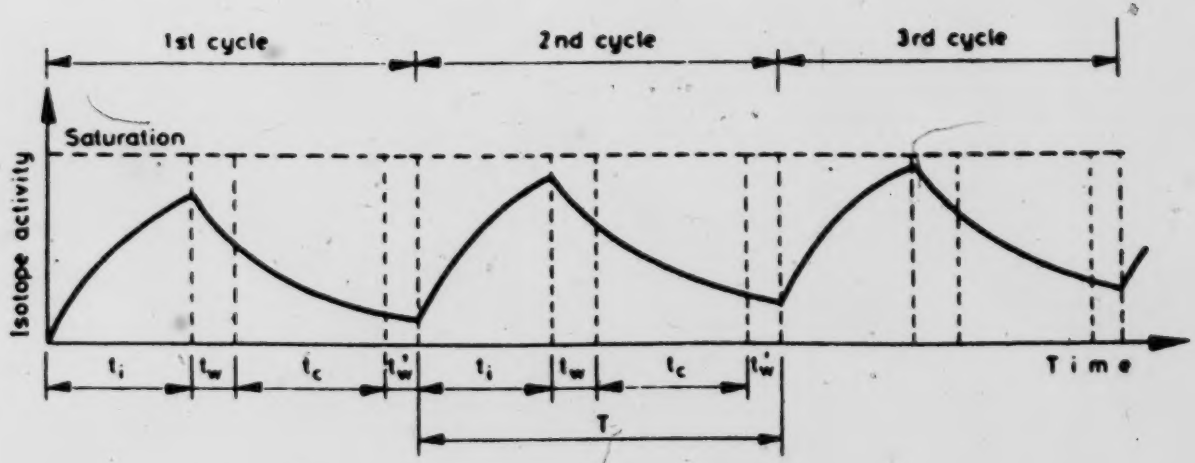

Figure 3.1.1 Isotope Activity as a Function of Time In a Cyclic Instrumental Neutron Activation Analysis Experiment[77].

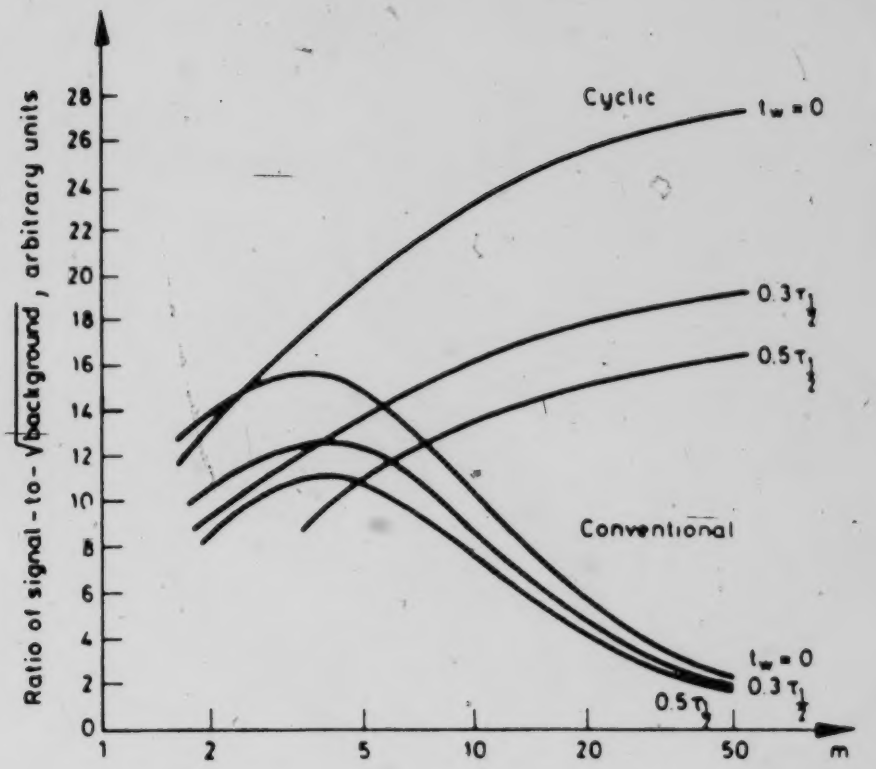

Figure 3.1.2 Variation of Cyclic and Conventional Signal-to-Noise (Signal-to-√Background) Ratios With Total Experimental Time For Various Waiting Periods[79]. The half-life of the predominant isotope in the background underlying the signal is assumed to be 100 times the half-life of the isotope of interest.

applied to radioisotopes with half-lives long enough to make conventional INAA feasible[80,81].

3.1.2 Cumulative Detector Response

In CINAA the detector response is cumulative and the induced activity for v cycle periods is recorded. The detector response for the first counting period is

$$D_1 = Nf\sigma\phi I_\gamma\varepsilon(W/M)\,(1/\lambda)\,(1-\exp(-\lambda t_i))\exp(-\lambda t_w)\,(1-\exp(-\lambda t_c)) \quad 3.3$$

where N is Avogadro's number, f is the fractional abundance of target isotope (in atom percent), σ is the reaction cross section (in cm^2 where 1 barn equals 10^{-24} cm^2), ϕ represents the incident neutron flux (in n cm^{-2} s^{-1}), I_γ is the number of γ-rays per disintegration, ε is the detector photopeak efficiency including geometry factors for the gamma-ray being detected, W equals the mass of the target isotope present in the sample, M is the atomic mass of the target isotope and λ is the nuclear decay constant of the product isotope (s^{-1}).

During the second counting period, the detector will not only respond to the activity induced by the second irradiation but also to the residual activity from the first exposure. The number of counts recorded during this second period is

$$D_2 = D_1 + D_1 e^{-\lambda T}$$

$$= D_1 (1 + e^{-\lambda T}) \quad 3.4$$

Extension to the v^{th} counting period results in an equation of the form

$$D_v = D_1 (1 + e^{-\lambda T} + e^{-2\lambda T} + \ldots + e^{-(v-1)\lambda T}) \quad 3.5$$

where the last term may be equivalently represented as

$$1 + e^{-\lambda T} + e^{-2\lambda T} + \ldots + e^{-(v-1)\lambda T} = (1-e^{-v\lambda T}) / (1-e^{-\lambda T}) \qquad 3.6$$

For v successive cycle periods, the cumulative detector response is

$$D_{vT} = \Sigma D_i$$

and for the summation from i=1 to v

$$D_{vT} = D_1 * (1 / (1-e^{-\lambda T})) \Sigma(1-e^{-i\lambda T}) \qquad 3.7$$

Subdividing the summation results in

$$D_{vT} = D_1 * (1 / (1-e^{-\lambda T})) * (v-\Sigma e^{-i\lambda T})$$

$$= D_1 * (1 / (1-e^{-\lambda T})) * v-(e^{-\lambda T}(1-e^{-v\lambda T}) / (1-e^{-\lambda T})) \qquad 3.8$$

and leads to a cumulative detector response for all v periods

$$D_{vT} = D_1 * (v/(1-e^{-\lambda T}) - e^{-\lambda T}(1-e^{-v\lambda T})/(1-e^{-\lambda T})^2) \qquad 3.9$$

When $t_w=t_{w'}=0$ and $t_i=t_c=T/2$, equation 3.9 is maximised for a given total experimental time. Even though t_w and $t_{w'}$ can never be zero in practice, it is still possible to obtain a maximising condition. Thus, for a given total experimental time T_0 and waiting times t_w and $t_{w'}$, dependent upon the characteristics of the transfer system, values of v and T may be found that maximise the value of D_{vT}.

3.1.3 Computer Simulated Detector Response

In 1981, Tout and Chatt[82] investigated the optimum timing parameters for a number of short-lived nuclides in four different types of simulated

sample matrices. Based on equation 3.9, a computer program was written to theoretically estimate these values for a total experimental time of approximately 300 seconds. Their investigations revealed that if the half-life of the nuclide ($t_{1/2}$ < 25 s) of interest was less than 0.18 of that of the shortest-lived nuclide making a major contribution to the background, the matrix effect could be well approximated as resulting from just that one major contributing nuclide. In addition, by using a single value of t_i and t_c they also found that a number of short-lived nuclides could be simultaneously studied at close to their best detection limits. For example, when t_i=t_c=6 or 7 s and t_w=t_w'=1 s, half-lives in the range 3 to 22 seconds (or possibly more) could be studied. The optimum values for t_i and t_c were, however, dependent on t_w and t_w'. In a simulated bovine liver matrix, the optimum values of t_i and t_c for ^{77m}Se ($t_{1/2}$ = 17.4 s) were found to vary from 12 seconds (t_w=t_w'=0.5 s) to 23 seconds (t_w=t_w'=4.0 s) when ^{28}Al was considered as the major contributor to the background activity. Also, when these computed results were compared with their corresponding experimental values a difference of 5% or less was noted.

Experimental Details

3.2.1 Sample Pretreatment

Fifteen glass samples (section 2.2.1, excluding group B) provided by an RCMP forensic laboratory (Edmonton, Alberta) were analysed. Sample pretreatment prior to weighing was identical to that described in section 2.2.2.

3.2.2 Subsample Preparation

Increments of nominal mass 1 mg and 5 mg were taken from each glass sample for analysis by CINAA. In general, the actual subsample increments were within 10% of the nominal values. A Cahn Gram (Model G, using loop A and the 5-mg range setting) Electrobalance (Cahn Instrument Co., Paramount, California, U.S.A.), equipped with powder paper (glassine) pans, was employed to weigh out four subsamples at each increment level. The subsamples were then placed directly into the hollow caps of four, 400-μL polyethylene micro-centrifuge tubes (Beckman Microfuge Tubes) which had previously been positioned in the top of the tubes. The caps were heat sealed using a commercial unit supplied by AECL (Model #K9-044) and placed at the bottom of 1-mL polyethylene vials. The micro-centrifuge tubes were then cut in half, crosswise, so that the vials were just able to be capped. This prevented lengthwise movement of the tubes within the 1-mL vials. In addition, the tubes were firmly seated within an indentation in the cap of the vials to prevent side to side movement. The vials were then inserted into 7-mL polyethylene irradiation vials. The 1- and 7-mL polyethylene containers were produced by Olympic Plastics Company, Inc., Los Angeles, California, U.S.A.. Empty, 1-mL polyethylene vials, acting solely as spacers, were placed on top of the 1-mL polyethylene vials already present in the irradiation tubes. Heat sealing of the irradiation capsules was then performed. All the vials and micro-centrifuge tubes were nitric acid washed (25% volume/volume); care was taken to avoid skin contact with any of the polyethylene containers. All subsamples were analysed in triplicate with one week separating each analysis to allow for the decay of the various radionuclides. One blank, consisting of a polyethylene sample tube plus vials, was also analysed daily for each sample

increment level. The analysis of the blanks served solely to monitor the counting operation for any gross contamination or unusual background fluctuations. Consequently, blank correction of the subsample values was not performed. Irradiation and counting of the various subsamples was performed using a randomised block design.

3.2.3 Irradiation and Counting

The irradiation and counting operations were performed at the SLOWPOKE-2 reactor facility situated on the University of Alberta campus. Irradiation involved exposing the samples to a nominal neutron flux of 1 X 10^{12} n cm^{-2} s^{-1} in site #5 of the reactor. A recycle irradiation controller supplied by AECL commercial products was employed for the timing operations. The unit contained three electromechanical timers (irradiation, delay and counting timers) along with a recycle counter. The irradiation, delay and counting periods were respectively 25, 4 and 25 seconds for the 1-mg subsamples and 10, 4 and 10 seconds for the 5-mg subsamples. In each case the counting period refers to clock time. The number of cycles employed for each increment level was twelve. The counting times (clock and live times) were obtained using a quartz crystal located within the multichannel analyser. Proper switching of the MCA between the waiting and counting modes was under the control of a software (macro) program.

Prior to irradiation of the sample, the irradiation, delay and counting timers were set to the desired time intervals and the required number of cycles was selected on the recycle counter. Samples were pneumatically driven into the reactor core and the irradiation timer was started when a photodetector unit, at the top of the reactor, signalled the passage of a capsule.

At the end of the set irradiation time, the capsule was ejected to a mechanical pinstop where proper positioning of the sample was attained by leaving the compressed air on for a few seconds after the initial impact of the sample on the pinstop. A distance of approximately one centimetre separated the detector endcap and the middle of the irradiation vial. It was not possible to measure this distance precisely since counting of the sample was performed while the irradiation vial remained inside the sample transfer tubes. The sample was also aligned to approximately coincide with the centre of the detector crystal.

All counting was performed with an 86 cm^3 active volume EG&G ORTEC (Oak Ridge, Tennessee, U.S.A.) WIN-15 horizontal, closed end, coaxial Ge(Li) detector system (Model # 8101-1521W) operating at a bias supply of +3500 volts. In addition, a Nuclear Data (ND)-660 MCA along with an EG&G ORTEC 472A amplifier (with a coarse gain of 20, a fine gain of 9.40 and a shaping time of 1 μs) and an ND-575 ADC (2k conversion gain) were coupled to this unit. An MTN-Model 1000 (Mech-Tronics Nuclear, Addison, Illinois, U.S.A.) precision pulse generator module (operated at 60 Hz) with a minimum rise time and an attenuation factor of 2 was also included. The detector specifications included a relative efficiency of 18.5% (compared with the efficiency of a 7.5-cm diameter by 7.5-cm thick NaI(Tl) scintillation detector at 25.0 cm), a measured full width half maximum of 2.1 keV and peak-to-Compton ratio of 53 : 1 for the 1332-keV photopeak of ^{60}Co. A mixed radionuclide standardised solution (QCY-44, Amersham Corporation, Amersham, England) emitting a series of 11 principal γ-rays, well spaced in energy from 88 keV to 1.836 MeV, was used for calibration of the system. A two-point calibration was performed using the ^{137}Cs photopeak at 661.638 keV

and the ^{60}Co peak at 1332.464 keV. The counting system and timer were automatically activated when the delay timer reached zero. The hafnium photopeak at 216 keV was collected using a 2048 channel spectrum. Following counting, a delay time of 4 seconds elapsed before the sample was reinserted into the reactor core. After the preselected number of cycles had expired, the cumulative spectrum for 12 cycle periods was stored on floppy disks for later retrieval and analysis. The sample, at this point, was ejected to a sample storage area.

3.2.4 Spectral Correction and Analysis

Spectral peak searching was accomplished using a software program (PREP 10) supplied by Nuclear Data. The program was integrated into an ND-660 MCA system. Deadtimes of less than 10% were maintained for each subsample. Deadtime corrections[66,67] for the decay of short-lived radioisotopes in the presence of active, longer-lived isotopes such as ^{24}Na and ^{38}Cl along with a correction factor for random summing effects[68] (pulse pile-up), were calculated using an Apple Macintosh Plus computer with Microsoft Excel software and applied to the hafnium photopeak. The data were also normalised to either correspond to 1 or 5 mg of material. The resulting data, with a sample size of 4 for each glass, was analysed using the Statistical Package for the Social Sciences (SPSS-X) on the University of Alberta Amdahl mainframe computer. The program UANOVA was employed.

3.2.5 Homogeneity Investigations

The panes of glass obtained from Pittsburgh Plate Glass Canada and AFG Glass Incorporated, described in section 2.2.6, were studied. Sample

pretreatment and subsample preparation were performed as outlined in sections 3.2.1 and 3.2.2. However, only one subsample was removed from each corner of a pane at the two increment levels (1- and 5-mg). The irradiation, counting and spectral correction procedures, outlined above in sections 3.2.3 and 3.2.4, were also implemented. One change involved the use of a personal computer based system equipped with a multichannel analyser card (Aptec Engineering Limited, Downsview, Ontario, Canada) and accompanying software instead of the Nuclear Data-660 MCA system and macro programs.

Results and Discussion

3.3.1 Occurrence of Hafnium

In this study, hafnium was the only additional element that was discovered to be useful for the discrimination of various flat glasses. Hafnium enters the glass production process through its association with limestone and is also present in the mineral zircon (i.e. a zirconium silicate) found in sand deposits[83]. Zircon occurs world-wide; the beach sands of Australia (east coast), India (Kerala) and the United States (Florida, Oregon and North and South Carolina) contain particularly large quantities of this mineral[83,84]. Since the amount of hafnium present in any glass batch formulation would be very small, its concentration is not controlled by the manufacturer and is uniquely dependent on the particular raw materials employed.

3.3.2 Optimisation of the CINAA Experimental Parameters

Monitoring of the 216-keV γ-ray photopeak was found to be the most sensitive means for detecting hafnium. This photopeak energy did not, however, correspond to one particular Hf isotope but was a combination of two short-lived radionuclides, ^{178m}Hf (214 keV, $t_{1/2}$ = 4.3 s) and ^{179m}Hf (217 keV, $t_{1/2}$ = 18.6 s), with the latter providing the greater sensitivity under the cyclic conditions chosen.

In optimising the signal-to-noise ratio for this 216-keV photopeak, it was necessary to investigate several parameters in the CINAA scheme. Since the sample was not removed from the irradiation vial prior to counting, the geometry factor not only included the distance between the detector endcap and the sample but also the physical positioning of the sample before the detector. This latter concern required that the sample be reproducibly positioned in front of the detector and was precisely the reason for sealing the sample within the cap of a micro-centrifuge tube. Confined within this cylindrical compartment (2 mm in diameter and 4 mm in length) the sample is prevented from moving very far even upon impact of the irradiation capsule with the pinstop. Investigations studying this parameter revealed no statistically discernible difference between the number of counts obtained when samples were confined to the space within a micro-centrifuge cap (i.e. a slightly variable sample geometry) and samples that were immobilised by packing Whatman #2 filter paper (Whatman Limited, England) in the cap along with the sample. The total experimental time was limited to 300 seconds since no discernible improvement in the signal-to-noise ratio was noted for total experimental times between 250 and 350 seconds. Determination of the optimum values for the irradiation, delay and counting

times depends to a large extent on the composition of the accompanying sample matrix. In this case, the optimum values for these parameters were found to be 25, 4 and 25 seconds respectively for the 1-mg subsamples. A limitation, imposed by the irradiation controller, prevented delay times of less than 4 seconds from being investigated.

At this point it is of interest to recall the work of Tout and Chatt[82]. According to their research, the background activity of the flat glass samples could be approximated as being due solely to ^{28}Al which was also the case for their simulated bovine liver matrix. For this situation, Tout and Chatt predicted optimum irradiation and counting times of 23 seconds for waiting times of 4.0 seconds when considering a total experimental time of approximately 300 seconds for the analysis of ^{77m}Se ($t_{1/2}$ = 17.4 s). The results presented here for the optimum t_i and t_c values (25 seconds) for the hafnium photopeak with waiting times of 4.0 seconds and a total experimental time of 300 seconds appear to be in excellent agreement with this work. The fact that two different sample matrices are compared should not be of concern here as Tout and Chatt have clearly stated that their parameters can also be applied in the analysis of all samples except those which have a significant background contribution from a nuclide with a half-life less than that of ^{28}Al.

Optimisation of the signal-to-noise ratio for the 5-mg subsamples was not as critical. Thus, the timing parameters were chosen primarily on the basis of preventing the dead time of the detector from exceeding 10%. Also, the precision of the measurements obtained using CINAA generally improved as the number of cycles was increased. In this particular case, the relative standard deviation decreased from 9 to 4% as the number of cycles

increased from 1 to 10 when samples ranging between 1 and 5 mg were studied.

In correcting for the dead time of the detector, Spyrou and Kerr[78] employed an average dead time correction which was based on the specific counting period considered. This meant that a different dead time correction was applied to each accumulated single spectrum for the v cycle periods. After correction of the individual spectra, they were then summed to obtain the cumulative detector response. A slightly different approach was considered for this investigation. The cumulative detector response for the hafnium photopeak after 12 cycle periods was multiplied by an overall correction factor, calculated using the cumulative clock and live times. In essence, the cyclic spectrum was corrected or treated in the same manner as a conventional INAA determination. Ten glasses representing the four refractive index groups studied by CINAA with sample increments ranging between 1 and 5 mg were analysed with Spyrou and Kerr's method and the overall correction factor method. The results were in excellent agreement, with the maximum difference between the two methods being 0.2% for the hafnium 216-keV photopeak. As a result, the collection and correction of each individual spectrum prior to obtaining the cumulative detector response was considered to be unnecessary.

3.3.3 General Characterisation of the Data Set

The data set was characterised using several criteria and some of these criteria were used to justify assumptions required for the statistical analysis that followed. None of the glasses in this study exhibited any evidence for a deviation from normality when the Kolmogorov-Smirnov one-sample test

was performed. In each case, the four subsamples of a given glass were considered after the three repeated measurements on each subsample were averaged. Upon calculating the 60 %RSD values for the repeated measurements within a particular increment level, an overall average measurement uncertainty of 10.4% (average value range = $4.1\%_{C1}$ to $16.6\%_{C3}$) for hafnium at the 1-mg increment level was obtained. At the 5-mg increment level this overall average value decreased to 6.3% and the average value range extended from 3.1 (C1) to 12.7% (D1). This measurement uncertainty, however, did not include an estimate of the uncertainty associated with the weighing of the various subsamples. When ten repeated weighings of the same sample were taken within the space of an hour, a weighing uncertainty of 1.7 μg resulted. No additional variability was noted when the 10 measurements were obtained by taking one measurement per day over an 11 day period.

3.3.4 Statistical Data Analysis

Analysis of the hafnium data was carried out employing the overall statistical model introduced in section 2.3.3. Discussion of the importance of models, along with definitions of the individual model terms, appears in sections 2.3.3 and 2.3.4. In Table 3.3.1, a summary table of F-ratios for four refractive index groups, using the King-Henderson algorithm[70] as the mean square model, is presented for the analysis of hafnium. Since very strong evidence was available (i.e. a probability value of approximately zero) in each case for the Grand Mean possessing a nonzero value, it was excluded from these tables. Strong evidence was also found for a statistically discernible difference in the Size term between the various glasses in refractive index

Hypothesis Term : Glass
Error Term : Subsample (Glass)

Univariate F-Ratios for Hf

Refractive Index Group	F-Ratio	DF1	DF2	Probability
A	34.90	3	12	0.0000
C	649.79	2	9	0.0000
D	27.39	3	12	0.0000
E	2.07	3	12	0.1571

Hypothesis Term : Subsample (Glass)
Error Term : Repeat (Subsample, Glass)

Univariate F-Ratios for Hf

Refractive Index Group	F-Ratio	DF1	DF2	Probability
A	3.67	12	32	0.0016
C	2.56	9	24	0.0318
D	1.18	12	32	0.3362
E	4.19	12	32	0.0006

Hypothesis Term : Repeat (Subsample, Glass)
Error Term : Size * Repeat (Subsample, Glass)

Univariate F-Ratios for Hf

Refractive Index Group	F-Ratio	DF1	DF2	Probability
A	1.22	32	32	0.2896
C	0.70	24	24	0.8022
D	1.24	32	32	0.2758
E	0.63	32	32	0.9030

Table 3.3.1 Univariate F-Ratios, Degrees of Freedom and Probability Values For the Glass, Subsample and Repeat Terms of the Overall Statistical Model (A Group, n_D = 1.5171, C Group, n_D = 1.5157, D Group, n_D = 1.5168 and E Group, n_D = 1.5191).

groups C and D. This was not evident in groups A and E. Interpretation of these results is difficult, however, due to a confounding of effects. The differences and similarities noted above for the Size term may only be apparent since both the degree of homogeneity exhibited by hafnium as a function of sample increment size and the experimental conditions (i.e. the irradiation and counting times) under which the samples were analysed must be considered before interpretation of the results is possible. Unravelling of these two effects was not pursued since the comparison of samples in any practical investigation would be performed using comparable sample sizes. Investigation of the interaction effects was not considered for the same reason.

The Glass term indicated strong evidence for a statistically discernible difference in the hafnium levels of at least one glass within each of groups A, C and D. All of the glasses in group E were found, however, to exhibit similar hafnium levels. The Subsample term for groups A and E indicated strong evidence that the population mean responses for the glasses found within a particular group were different. Upon closer examination, one subsample appeared to deviate considerably from the rest of the subsamples at the 5-mg increment level for glass A1. An average value of 4474 counts for 3 repeated measurements was obtained for this subsample while the counts for the other 3 subsamples ranged between 3044 and 3221. In contrast to this, all of the E group glasses appeared to exhibit considerable variability in their hafnium levels when 1-mg subsamples were taken.

Based on the above observations, further study of the glasses in group A (i.e. more data) would be warranted to determine definitely whether the hafnium values for certain subsamples were actually discernible from other

subsamples taken from the same glass. However, since the probability value for the Subsample term (0.0006) for the E group glasses was quite small, there was strong evidence to support the hypothesis that these glasses were not homogeneous with respect to their hafnium contents. Therefore, it is strongly suggested that a number of subsamples should be taken to obtain a more reliable estimate of the hafnium contents of these glasses. And finally, none of the glasses showed any evidence for a difference in their elemental mean responses when the Repeat term was investigated. Thus, repeated measurements on the same subsample indicated that the variability associated with the measurement technique did not discernibly aid in the discrimination of glasses found within the same refractive index group.

Pairwise comparisons of the various glasses found within a specific RI group were undertaken. The determination of statistically discernible differences in the hafnium content of these glasses was obtained by employing Tukey's alternate multiple comparisons procedure (Tukey B). The hypothesis term for the comparisons was Size * Glass and an experimentwise error rate of 0.01 was utilised. Since the model equation for the Tukey B procedure was Size * Glass, this represented a fixed effects model. The additional use of equal sample sizes for the comparison of the various glasses meant that the statistical tests in this section were reasonably insensitive to deviations from the homogeneity of variance assumption[73]. This is important because analyses where both of these conditions do not apply must consider the possibility of heterogeneous variances when a pooled variance term is utilised. Failure to account for this heterogeneity may result in a situation where the type I error is dramatically increased beyond the level to which an experimenter believes it is controlled.

Presented in Table 3.3.2 are the results of the pairwise comparisons for the various glasses using the Tukey B procedure. The quoted probabilities, due to a limitation of the program UANOVA, were obtained by means of the least statistically discernible difference procedure (pairwise error rate). Although the probability values obtained in this manner are not absolutely correct, the two methods agree on which comparisons resulted in statistically discernible outcomes. Hence the quoted probabilities should provide an excellent approximation of the actual probability values. Only in one instance did a discrepancy arise between the two procedures. This resulted upon comparison of glasses A1 and A3 at the 5-mg increment level. In this case, the Tukey procedure indicated a statistically discernible difference at the 1% significance level while the LSDD method found no difference between the two glasses. The difference arose from the critical values chosen. A critical value of 2.70 was employed in the Tukey procedure while the LSDD method utilised a critical value of 2.80. Therefore, a wide discrepancy was not noted between the two methods. However, since the probability value was very close to the 1% significance level, further study of these two glasses would be warranted to determine with more assurance whether these two glasses were actually discernible based on their hafnium levels. Also appearing in Table 3.3.2 are the results of a classical t-test for the difference between two means using a pooled (weighted average) variance term. These have been included to provide a more complete evaluation of Tukey's multiple comparisons procedure. In general, only minor discrepancies were noted between the two methods for the analysis of hafnium.

Overall, at the 1-mg increment level 33% of all the pairwise comparisons between glasses possessing the same RI were distinguishable on

	Probability Values			
	1-mg Subsamples		5-mg Subsamples	
Hf Comparison	Tukey B	t-test	Tukey B	t-test
A1 vs. A2	NSD	+	***	NSD
A1 vs. A3	NSD	NSD	*	NSD
A1 vs. A5	*	+	***	++
A2 vs. A3	NSD	+	*	++
A2 vs. A5	NSD	NSD	*	++
A3 vs. A5	*	+	***	++
C1 vs. C2	NSD	NSD	NSD	NSD
C1 vs. C3	***	++	***	++
C2 vs. C3	***	++	***	++
D1 vs. D2	*	NSD	***	++
D1 vs. D3	**	+	***	++
D1 vs. D4	**	+	***	++
D2 vs. D3	NSD	NSD	NSD	+
D2 vs. D4	NSD	NSD	NSD	NSD
D3 vs. D4	NSD	NSD	NSD	NSD
E1 vs. E2	NSD	NSD	NSD	+
E1 vs. E3	NSD	NSD	NSD	+
E1 vs. E4	NSD	NSD	NSD	NSD
E2 vs. E3	NSD	NSD	NSD	NSD
E2 vs. E4	NSD	NSD	NSD	NSD
E3 vs. E4	NSD	NSD	NSD	+

NSD = Not Statistically Discernible
\+ 0.001 < probability < 0.01
++ probability < 0.001

* 0.001 < probability < 0.01
** 0.0001 < probability < 0.001
*** probability < 0.0001

Table 3.3.2 Tukey B and t-test Probability Values For Pairwise Comparisons of the A, C, D and E Glasses Using Four 1-mg or Four 5-mg Subsamples of Each Glass.

the basis of their hafnium content when a 1% experimentwise error rate was used. This rose to 52% at the 5-mg increment level. In general, the differences noted were more marked for the 5-mg subsamples, with 8 of the 11 statistically discernible comparisons yielding probability values of less than 1 in 10,000. Only two of these comparisons remained at this probability level when 1-mg subsamples were considered. Consideration of glasses A1, A2, A3, D2, D4, E2, E3 and E4 revealed that hafnium did not appear to be a good element for the discrimination of float glasses. Only the A glasses were distinguishable from one another using Tukey's procedure when 5-mg subsamples were taken. It was also found that no additional discrimination of the fifteen glasses was provided by hafnium when results were compared with the Na, Al and Ca data.

3.3.5 Analysis of Float Glass Panes

The levels of hafnium within different panes produced by two major Canadian flat glass manufacturers may be summarised as follows. For both manufacturers there was no evidence to indicate any deviation from normality when the within-pane results were studied using the Kolmogorov-Smirnov one-sample test. When within- (using the Studentized Range Test at a 10% significance level) and between-pane comparisons (using ANOVA tables at a 5% significance level) were made, for 1- and 5-mg subsamples, the panes produced by a given manufacturer were found to be homogeneous. This homogeneity also indicated the consistency associated with the production process since the panes were produced at different times from different batches. As a result of this finding, percent relative standard deviation values (i.e. analytical uncertainties) were calculated for the

determination of hafnium at both subsample increment levels for the manufacturers. A %RSD of 25.1 and 17.1% were obtained for the AFG- and Pittsburgh-produced panes at the 1-mg increment level. These values decreased to 16.8 (AFG) and 14.7% (Pittsburgh) for 5-mg subsamples. Further, the average hafnium levels in the glass samples produced by each manufacturer (1-mg subsamples 2370 (AFG) and 2786 (Pittsburgh) counts, 5-mg subsamples 2153 (AFG) and 2689 (Pittsburgh) counts) showed no statistically discernible difference at the 1% significance level for either of the increments. The average values were based on 16 analyses (4 measurements on each of 4 panes) of the AFG-produced panes and 24 analyses (4 measurements on each of 6 panes) of the Pittsburgh panes. A t-test of the difference between two means utilising a weighted average of the variances of these two samples was employed to make this comparison. Comparison of the panes of glass, which had a known origin, to those glasses provided by the RCMP was also performed. These comparisons showed 6 of the 15 glasses to be statistically discernible, at the 5-mg increment level, from the Pittsburgh-produced glass. This value rose to 7 out of 15 for the AFG panes.

Chapter 4

Introduction

4.1.1 The Epithermal Instrumental Neutron Activation Analysis Experiment

A material possessing an extremely large thermal neutron capture cross section (e.g. 19910 barns for ^{113}Cd or 3837 barns for ^{10}B) is employed in epithermal instrumental neutron activation analysis (EINAA) to effectively limit the exposure of a sample to thermal neutrons. As a result of this screening the activities of the more abundant elements such as sodium and aluminum, which would normally activate readily in a predominantly thermal neutron flux, are suppressed relative to those elements activated by epithermal neutrons. Thus, photopeaks which would normally be obscured by the Comptons associated with these readily activated species produced in thermal neutron capture reactions are enhanced under the EINAA scheme. The use of epithermal neutrons, which participate primarily in the resonance (n,γ) and lower cross section (n,p) reactions, may also prove advantageous for elements that either have too long a half-life for the produced radionuclide or do not emit γ-rays for thermal (n,γ) reactions. Although epithermal neutron activation strictly involves both epithermal and fast neutrons, interfering reactions due to the fast neutrons are normally of little consequence since they only interact with the filter to a small extent. Neutron capture cross sections for thermal and epithermal neutrons are on the order of barns (10^{-24} cm^2) whereas the cross sections for fast neutrons are generally in the millibarn range.

4.1.2 Thermal Neutron Filters

The most common thermal neutron filters are cadmium, boron and a combination shield material made of cadmium and boron. Filters made with cadmium, manganese oxide, manganese bromide and sodium chloride[85] and with cadmium, manganese chloride and sodium chloride[86] have also been investigated, but generally no readily apparent advantage has been demonstrated by these more elaborate filters[87]. Although cadmium was the original shielding material employed, many investigators now use boron. Boron is convenient since it is not readily activated, unlike cadmium, and thus permits reuse of the same filter repeatedly along with easy handling of the filter for the assay of short-lived radionuclides. Boron is also advantageous from a health physics point of view since it reduces the risk of exposure of laboratory personnel to excessive radiation fields. While cadmium is essentially opaque to neutrons with kinetic energies of less than about 0.5 eV, boron follows a 1/v dependence (i.e. the activation cross section is inversely proportional to the neutron velocity) and only approaches this level at approximately 280 eV as shown in Figure 4.1.1. Consequently, boron provides a greater reduction in the activities from the more abundant elements which have excitation functions in the lower epithermal region (1 to 10 eV). In addition, the large 1/v neutron capture cross section of ^{10}B, which extends well into the resonance region, effectively reduces the resonance flux reaching a sample. This is an advantage since many of the more abundant elements also have large resonances in this region. Also, by using boron the care needed in the fabrication of cadmium metal irradiation containers, due to the toxicity of cadmium, is avoided. Recently, a combination of shielding materials has been utilised[89,90]. The sample,

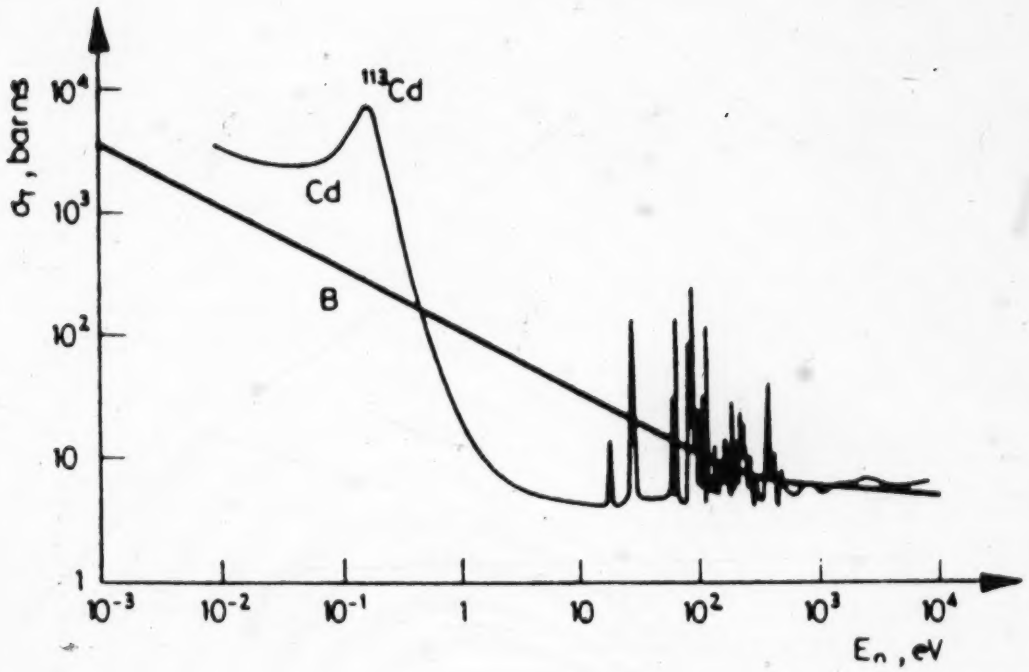

Figure 4.1.1 Dependence of Absorption Cross Section on Neutron Energy For Boron and Cadmium[88].

surrounded by a boron filter, is placed inside an irradiation capsule. The capsule is then irradiated in a cadmium lined site which is permanently installed in the reactor core.

4.1.3 Fabrication of Boron Filters

A variety of techniques have been used to fabricate boron filters. The use of polyethylene-boron materials as thermal neutron absorbers has been investigated[51]. The shields were machined from bricks which contained 5% boron powder and 30% boron in the form of boron carbide powder. Short irradiation periods were used since some melting and fusing of the material was noted. This was attributed to the tremendous amount of energy deposited in the polyethylene matrix by the recoil energy of the products involved in the $^{10}B(n,\alpha)^{7}Li$ reaction. Deterioration of the polyethylene matrix was noted upon repeated short exposures with accumulated neutron doses in excess of about 10^{17} neutrons per square centimetre. Sintered boron nitride filters were employed by Chisela et al.[91] and Jones and co-workers[92] while Bem and Ryan[93], although not explicitly stated, apparently[94] embedded the BN in paraffin wax. These workers found BN suitable for short irradiations (irradiations up to approximately an hour were considered) but Ehmann and co-workers[95] have warned against using this filter for longer periods of time. Of particular concern was the relatively high cross section of 1.81 barns for the $^{14}N(n,p)^{14}C$ reaction and the formation of an appreciable amount of the long-lived radionuclide ^{14}C.

This difficulty was avoided by using boron carbide. Neutron capture reactions on ^{12}C produce ^{13}C, which has a thermal neutron cross section of only 0.9 millibarns. However, the production of B_4C filters has been

particularly challenging since this material is exceedingly abrasive, and causes excessive wear of both high speed steel and tungsten carbide tools. Parry[96] along with Cesana and co-workers[87], used two coaxial cylinders, the external made of aluminum and the internal of cadmium, with the volume between the cylinders being filled with boron carbide. Chisela et al.[91] used sintered B_4C absorbers, while Ehmann and researchers[95] used surplus rocket nozzles. Ehmann has suggested the use of wall thicknesses of 4 mm since 2-mm thick walls were found to be brittle. Stuart and Ryan[94] along with Bem and Ryan[93] produced B_4C filters embedded in paraffin wax. They also employed wall thicknesses of 4 mm but as noted they found this type of shield suitable only for a low temperature reactor such as the SLOWPOKE-2. Bem and Ryan also constructed boron shields in the same fashion out of B_2O_3 and enriched boron powder (92.94% enriched in ^{10}B). Kennedy and Touhouche[97], on the other hand, embedded B_4C in an epoxy resin to make their thermal neutron filters.

Another parameter to be considered in the construction of boron filters is the boron thickness or boron surface density. This parameter is important because variation of the boron thickness results in different cutoff energies (i.e. the probability of various reactions occurring are reduced below this energy due to absorption of the neutrons by the filter). By manipulation of these cutoff energies greater selectivity for various elements may be afforded. Rossitto and co-workers[98] considered cadmium, boron, and cadmium plus boron shields of varying thicknesses. They concluded that the most appropriate filter for resonances less than about 2 eV was cadmium. For resonances extending from 2 eV up to 15 eV a cadmium plus boron filter was better than a cadmium shield, but at energies greater than 15 eV, boron and cadmium plus boron were equally effective when the filter thickness was

optimised. This optimisation was based on the best improvement of the ratio, using a particular thermal neutron filter, of the activity of interest to the most common major element (^{24}Na and ^{28}Al are employed for biological and geological samples respectively) present in the matrix. This ratio is commonly referred to as the advantage factor (AF), which may be expressed as

$$AF_x = A_X / A_{Na} \qquad 4.1$$

where A_X is the activity for the nuclide of interest and A_{Na} is the activity for sodium when, for example, a boron carbide filter material is used. Bem and Ryan[93] found for a majority of elements that the 12 eV energy cutoff was better in terms of the advantage factors than a 20 eV cutoff. This effect results beyond a certain boron thickness since these thick filters exhibit an increased absorption of high-energy neutrons. In subsequent work done by Stuart and Ryan[94], a natural boron shield with an energy cutoff of 10 eV was found to be the most useful filter for enhanced detection of trace elements with short-lived nuclides.

Experimental Details

4.2.1 Fabrication of Boron Carbide Inner Site Shields

Methyl methacrylate (Eastman Kodak Company, Rochester, New York, U.S.A.) was distilled twice from sodium hydroxide to remove any hydroquinone or quinol (boiling point = 285 °C) which was added as a preservative to prevent polymerisation of the monomer. Addition of azoisobutyronitrile (2, 2'-azobis (2-methylproprionitrile) or AIBN, a free radical initiator, Aldrich Chemical Company, Inc., Milwaukee, Wisconsin,

U.S.A.) resulted in a 3% (weight/volume) AIBN-methyl methacrylate solution. This solution was then placed in a sonicator for approximately 10 to 15 minutes. The mold for the shield consisted of a 3-cm thick teflon block in which a central 6.25 mm diameter hole had been drilled to a depth of 1.5 centimetres. A 13.75 mm inner diameter concentric groove was also cut in the teflon block to the same depth. Glass tubing, approximately 24 cm in length, was inserted in this groove and Plastacine was used to seal the gap that remained between the glass and teflon. A methyl methacrylate or nylon rod, approximately 6 mm in diameter, was positioned in the central hole of the block and proper alignment of the rod and tube was attained using paperclips. Once the rod and outer glass tubing had been secured, the AIBN-methyl methacrylate solution was carefully poured in, followed by the boron carbide powder (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, U.S.A.). Addition of the powder was continued until it came within approximately 3 mm of the top of the AIBN-methyl methacrylate solution. The entire assembly was then placed in a sonicator for 15 minutes and more B_4C was added at the end of the time period. Sonication was continued for a further 15 to 20 minutes. This resulted in approximately a 3 : 1 boron carbide to methyl methacrylate solution ratio. At the completion of this period, the entire assembly was placed in a 1-litre graduated cylinder and water (~ 56 °C) was added until the water level was above the top of the B_4C-methyl methacrylate solution. The 1-litre graduated cylinder was placed in a 56 °C water bath overnight. Solid B_4C rods were made in the same manner, using as a form glass tubing with an inner diameter of approximately 6 or 13.75 millimetres.

The ends of the boron carbide stock material, containing the methyl methacrylate rod, were cut off with a diamond circular saw. A length

corresponding to the main body of the thermal neutron shield was removed by the same means. The methyl methacrylate rod was then drilled out to complete the fabrication of the filter body. Cutting of the solid B_4C rod stock was performed in the same manner for fabrication of the top and bottom covers of the shield. The main body of the shield was 13.75 mm in diameter, with a 6.25-mm (diameter) central channel, and 31.5-mm long. Minimisation of the neutron flux perturbation was the principal concern in the design of the shield body length. The top cover was 13.75 mm in diameter and 2-mm thick. Centred on this cover was a 6.20-mm (diameter) by 1.75-mm (thick) plug of solid B_4C rod stock. Cyanoacrylate glue (Super Jet$_{TM}$, Carl Goldberg Models, Inc., Chicago, Illinois, U.S.A.) was used to secure these pieces. Designed to fit within the central channel of the shield body, the plug prevented displacement of the cover while the sample was in transit. The bottom cover of the shield was made in exactly the same manner as the top cover but was attached to the shield body using cyanoacrylate glue. Previous investigators[92,95] have employed a comparable shield design.

4.2.2 Sample Pretreatment

The nineteen glass samples (section 2.2.1) provided by an RCMP forensic laboratory (Edmonton, Alberta) were analysed. Sample pretreatment prior to weighing was identical to that described in section 2.2.2.

4.2.3 Subsample Preparation

One or two subsamples, ranging between approximately 100 and 500 μg, were taken from each glass sample for analysis by EINAA. A Cahn Gram (Model G, using loop A and the 1-mg range setting) Electrobalance (Cahn

Instrument Co., Paramount, California, U.S.A.), equipped with powder paper (glassine) pans, was employed. The subsamples were then placed directly into four nitric acid washed (25% volume/volume) 400-µL polyethylene micro-centrifuge tubes (Beckman Microfuge Tubes) which had been previously cut in half crosswise. Care was taken to avoid skin contact with the micro-centrifuge tubes. The tubes were heat sealed using a commercial unit supplied by AECL (Model #K9-044) and trimmed to ensure that they would fit within the B_4C shield. After trimming, the tubes were deposited in 7-mL polyethylene irradiation vials. The 1- and 7-mL polyethylene containers were produced by Olympic Plastics Company, Inc., Los Angeles, California, U.S.A.. Blanks were also prepared and analysed on a daily basis.

4.2.4 Irradiation and Counting

The irradiation and counting operations were performed at the SLOWPOKE-2 reactor facility situated on the University of Alberta campus. Prior to irradiation in site #1, the micro-centrifuge tube containing the subsample of glass was placed inside the B_4C shield. The shield was then placed in the irradiation tube and a trimmed, empty, 1-mL polyethylene vial (15.25 mm long), acting solely as a spacer, was placed on top of the shield. Irradiation involved exposing the subsamples to a nominal neutron flux of 1 X 10^{12} n cm^{-2} s^{-1}. The irradiation, delay and counting periods employed were respectively 10, 1 and 10 minutes. In this case the counting period refers to live time. Timing of the irradiation was performed by a digital LED counter which was part of the SLOWPOKE-2 irradiation controller supplied by AECL commercial products. The delay time was obtained via a stopwatch and the counting times (clock time and live time) were obtained by employing a

quartz crystal located within the MCA. Prior to positioning of the sample before the detector, the micro-centrifuge tubes were shaken to ensure that the sample was located at the bottom of the tube. Sample placement was at a distance of 1 cm from the detector in a cave which had 10-cm thick lead walls. The height of the cave was 39 cm while the width and length were both 30 cm (internal dimensions). A plastic collar which fit around the detector had a plastic sample rack attached to it. Slots in the rack allowed for precise positioning of the sample card so that the card was held parallel to the endcap of the detector. The plastic sample card contained concentric polyethylene rings which fit snugly around the sample tube. The bottom of the sample tube was aligned to coincide with the centre of the detector crystal.

All counting was carried out with a Model 20180 EG&G ORTEC (Oak Ridge, Tennessee, U.S.A.) horizontal, closed end, hyper-pure (p-type) germanium, coaxial detector system operating at a bias supply of +3500 volts. In addition, a Nuclear Data (ND)-660 multichannel analyser along with an EG&G ORTEC 572 amplifier (coarse gain of 20 and a shaping time of 3 μs) and an ND-575 ADC (4k conversion gain) were coupled to this unit. An EG&G ORTEC 419 precision pulse generator module (operated at 75 Hz) with a minimum rise time and an attenuation factor of 2 was also included. The detector specifications included a relative efficiency of 22.4% (compared with the efficiency of a 7.5-cm diameter by 7.5-cm thick NaI(Tl) scintillation detector at 25.0 cm), a measured full width half maximum of 1.71 keV and peak-to-Compton ratio of 59.3 : 1 for the 1332 keV photopeak of ^{60}Co. The full width tenth maximum to full width half maximum ratio (FWTM/FWHM) and the full width fiftieth maximum to full width half maximum ratio (FWFM/FWHM) were 1.84 and 2.43 respectively. These ratios reflect the

quality of the peak shape, since a Gaussian curve possesses a FWTM/FWHM ratio of 1.82 and a FWFM/FWHM ratio of 2.38. All detector specifications are quoted for a 6-μs amplifier time constant. A mixed radionuclide standardised solution (QCY-44, Amersham Corporation, Amersham, England) emitting a series of 11 principal γ-rays, well spaced in energy from 88 keV to 1.836 MeV, was used for calibration of the system. A two-point calibration was performed using the ^{109}Cd photopeak at 88.037 keV and the ^{60}Co sum peak at 2505.672 keV. The measured radioisotope signals were collected using a 4096 channel spectrum and were stored on floppy disks for later retrieval and analysis.

4.2.5 Spectral Correction

Spectral peak searching was accomplished using a software program (PREP 10) supplied by Nuclear Data. The program was integrated into an ND-660 MCA system. Deadtimes of less than 1% were obtained for each subsample. Deadtime corrections[66,67] and a correction factor for random summing effects[68] (pulse pile-up) were calculated, using an Apple Macintosh Plus computer with Microsoft Excel software, and applied to each peak. The data were also normalised to correspond to 100 μg of material.

Results and Discussion

4.3.1 Evaluation of the Boron Carbide Shield

The production of the B_4C shield was fairly simple and straightforward. Embedding of the B_4C in a polymethacrylate matrix resulted in a shield that was relatively robust with respect to the operating temperature of the reactor. Specifically, its use would not be limited to the low temperatures of, for

example, a SLOWPOKE reactor as is the case for a shield having paraffin wax as the matrix material. In addition, the heat generated by neutron capture reactions does not restrict its use to outer irradiation sites or lower neutron fluxes in a SLOWPOKE reactor.

Initially, irradiation of the shield (461 mg B/cm^2 or an approximate neutron energy cutoff of 15 eV[98]) was performed. A nominal neutron flux of 1 X 10^{12} n cm^{-2} s^{-1} was employed but insertion of the shield in the reactor core resulted in a decrease of approximately 15% in this value[99]. After a 10-minute irradiation, the following γ-radiation fields (mR/h) at the surface of the shield, with the time after irradiation indicated in brackets, were noted : 3.0 (30 seconds), 2.1 (1 minute), 1.1 (4 minutes), 0.3 (20 minutes), 0.1 (1 hour) and a background level reading (24 hours). Concurrent with this study, a γ-ray spectrum was acquired. Qualitative analysis of the spectrum revealed the presence of Mn, Na, V, Cl, Al and W which have also been observed by Bem and Ryan[93]. In addition to these elements, our study revealed Mg, Cu, Ca and Ti. This may have resulted because a nominal flux higher by a factor of two was employed in this investigation. Overall, the activity induced in the B_4C shielding material along with the type of impurities present appear to be comparable with the work of Bem and Ryan.

To determine the reduction in the sodium and aluminum values when a B_4C shield was employed, a study of nineteen glass samples provided by the RCMP was initiated. The analysis in all cases consisted of a 10, 1 and 10 minute irradiation, delay and counting scheme. Prior to use of the filters, average sodium values for 3 repeated measurements on each of 4, 100-μg subsamples of a glass (see section 2.2.3) ranged between 6832 and 8300 counts. Shielding of the sample resulted in at least a 98.8% reduction in the number

of counts observed for either of the sodium photopeaks. Reduction of the aluminum signal was not as large and ranged between 69.9 and 93.2% when 100-μg glass samples were considered. Without the shield, the average number of counts (3 repeated measurements on each of 4, 100-μg subsamples of a glass, see section 2.2.3) were found to be between 1673 and 7083 but using the shield resulted in a spread of only 153 counts (412 to 565). The $^{28}Si(n, p)^{28}Al$ reaction was believed to be responsible for preventing any further reduction in the intensity of the aluminum photopeak. Irradiation of an 879.8-μg sample of SiO_2 (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, U.S.A., 99.999% SiO_2 with 4 to 8 ppm of Al present) and a 691.6-μg sample of $Al_2(SO_4)_3$ (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, U.S.A., 99.999% $Al_2(SO_4)_3$ with 0.5 to 2 ppm of Si present) was performed to test this theory. A calculation based on a glass sample containing 72% by weight SiO_2 and 1% by weight Al_2O_3 yielded 472 counts for the $^{28}Si(n, p)^{28}Al$ reaction while only 19 counts resulted from the $^{27}Al(n, \gamma)^{28}Al$ reaction. Therefore, it does appear that the $^{28}Si(n, p)^{28}Al$ reaction is primarily responsible for the counts present in the 1779-keV photopeak of aluminum when a B_4C filter is employed. This study also confirmed the excellent performance of the shields for reduction of contributions made by sodium and aluminum to the background.

4.3.2 Analysis of Flat Glass Samples

Analysis of the nineteen glass samples resulted in the identification of only two elements which were above Currie's limit of determination[69]. The elements were aluminum and silicon. Since the silicon content of flat glasses is known to be relatively invariant[100-102], further subsample and repeat

determinations on each glass were not performed. Other elements found to be measurable, but at levels below Currie's L_Q value, were Mg, Mn, Na, Al and Ca. It is important to note here that even a significant reduction in the background levels, when compared to a conventional INAA experiment, did not reveal any additional elements in the flat glass samples. This reinforces the idea that modern flat glass production is a well controlled process.

During the course of this work, a difficulty associated with the design of the boron carbide shield became evident. Despite having a plastic capsule on top of the cover to cushion the impact of transporting the sample to and from the reactor core, the edges of the top cover cracked and replacement was generally necessary after 8 to 10 hours of use. The problem resulted from the fact that the cover was only 2 mm thick to allow for a plug thickness of 1.75 millimetres. Modification of the cover was not attempted but a thicker cover, while maintaining the overall dimensions of the cover and plug, could possibly alleviate this problem.

Chapter 5

Summary and Future Directions

5.1.1 Summary

In a court of law, a forensic scientist will generally be asked two questions with regard to glass submitted as evidence. The first deals with the identification of the type of glass (i.e. classification) while the second concerns the matching of the suspect and control glass samples (i.e. discrimination).

Refractive index measurements have been used extensively over the years to characterise various glasses. Despite being an excellent discrimination test, the use of refractive index measurements to classify glasses is limited because the RI distributions of flat and container glasses overlap significantly[103]. Other attempts at classifying various glasses by means of physical measurements (e.g. looking for the 3 refractive indices[104,105] or the fluorescence[38] exhibited by float glasses and the use of interference objective lenses in microscopy to determine whether the fragment of glass bears an original surface of the parent object[106-109]) have all met with limited use over the years. The fluorescence of float glass samples has also been used to differentiate between float and nonfloat window glasses as well as between different samples of float glass. This method has also found little application.

The bulk of the present work concerned with the classification and discrimination of glass samples has dealt with their elemental composition. In the past, numerous techniques have been employed (SSMS, XRF, SEM,

AA, etc.) but it appears now that ICP-AES is emerging as the dominant method for this purpose. However, despite the impressive sensitivity of the technique, its ability to discriminate among flat glass samples is hampered by the low precision associated with most determinations[42-44]. Poor discrimination may also be attributed to the fact that most of this work was carried out in the United Kingdom on flat glass produced by a relatively limited number of manufacturers.

The research embodied in this thesis has addressed the elemental discrimination of flat glasses using several instrumental neutron activation analysis techniques. In general, instrumental neutron activation analysis is attractive for forensic purposes because the technique is nondestructive and allows further analyses, by the same or different methods, to be performed on the same glass test portions. This is particularly important when only a small sample (generally from the suspect) is available. In addition, using nondestructive techniques also preserves the sample for presentation in court. Coupled with the nondestructive nature of the technique is a fairly straightforward sample treatment procedure in which the sample is simply cleaned and weighed prior to irradiation. Many elements are capable of being detected and identified with high sensitivity and selectivity because advantage can be taken of differences in both half-lives and γ-ray energies. Simultaneous detection of many elements is possible, and since most elements possess several radioactive isotopes, a choice between detecting either a short or long-lived radionuclide is often available. Comparison of samples by means of their γ-ray spectra without the need for quantitative comparison to elemental standards is another advantage. And finally, the fact that the technique may be automated permits high sample throughput. Often

the lack of availability of nuclear reactors and the cost per analysis are cited as disadvantages associated with the technique. In Canada, however, small pool-type nuclear reactors (SLOWPOKE's) developed by Atomic Energy of Canada Limited are located at universities across the country. The cost for analyses performed at these facilities are competitive with commercial rates charged by contracting laboratories.

In this investigation nineteen glass fragments (18 of which were flat glasses) representing five refractive index groups were analysed. Employing instrumental neutron activation analysis, the Subsample and Repeat terms of the overall statistical model did not make a statistically discernible contribution to the differences noted between the glasses found within a particular refractive index group when a 1% experimentwise error rate was used. Further study of the Subsample term for the glasses in one of the groups (group D) is warranted, however, since the probability value associated with the univariate F-ratio for aluminum was only 0.0096.

Pairwise comparison between glasses possessing the same refractive index (3 repeat measurements on each of 4 subsamples for every glass) resulted in 90% of all the comparisons being distinguished at the 1-mg increment level when a 1% experimentwise error rate was employed. At the 100-μg level, 73% of all pairwise comparisons were distinguishable. When a t-test was employed for the comparison of 4 subsamples from a control glass with 1 subsample from a suspect (one measurement per subsample in both cases), 50% of all the pairwise comparisons at the 1-mg increment level resulted in discrimination at the 1% significance level (pairwise error rate). Only 26% of all comparisons resulted in discrimination of the glasses within a particular RI group at the 100-μg level. Aluminum was found to be the best

element for discriminating between the various glasses, followed by sodium and then calcium. No apparent difference between the information provided by the two sodium photopeaks (1369 and 2754 keV) was noted despite their location in different parts of the γ-ray spectrum. Tukey's alternate multiple comparisons procedure appeared to be more sensitive to deviations in the levels of the elements for the glasses than a classical t-test.

Comparison of glass B1 (tumbler) to the other 18 glasses indicated its calcium and aluminum values were very distinctive and gave the highest average values for any of the 19 glasses at both increment levels. For the ten glasses that were determined by their fluorescent properties to be float glasses, only one out of eight pairwise comparisons could not be distinguished on the basis of any of the studied elements at the 1-mg increment level. When the results were considered for the 100-μg increment level, only 4 of the 8 possible pairwise comparisons remained statistically discernible.

Consideration of a series of panes produced by either of two major Canadian flat glass manufacturers revealed the distribution of sodium, aluminum and calcium within the panes to be homogeneous at both the 1-mg and 100-μg increment levels. The glass formulations used by each manufacturer were found to be readily distinguishable from one another on the basis of their aluminum and calcium contents. Analysis of the panes also provided an estimate of the precision associated with the INAA technique. The %RSD values at the 1-mg increment level for Na-1 (1369 keV), Na-2 (2754 keV), Al and Ca for 16 and 24 analyses respectively on the AFG/Pittsburgh glass samples were 1.2/2.2, 1.8/2.5, 1.7/3.6 and 4.2/5.5. At the 100-μg increment level these values rose slightly, in general, and attained values of 2.1/2.4, 2.4/2.6, 3.4/11.8 and 5.5/8.8 for Na-1, Na-2, Al and Ca. Further, upon

comparison of the nineteen glass samples with the panes produced by the Canadian manufacturers, it appeared unlikely that any of the glass fragments provided by the RCMP were produced by either of the manufacturers studied in this investigation.

Employing cyclic instrumental neutron activation analysis (CINAA), hafnium was the only additional element found useful for the discrimination of flat glasses. Optimisation of the signal-to-noise ratio in CINAA involved the study of several parameters. Since no statistically discernible difference was noted between the number of counts obtained by confining the sample to the hollow cap of a micro-centrifuge tube as opposed to rigidly fixing the position of the sample within the cap, the former condition was used. A total experimental time of 300 seconds was found to be optimal for the detection of hafnium in the flat glass samples studied. Optimum values for irradiation, delay and counting times for the 1-mg subsamples were 25, 4 and 25 seconds. Five-milligram subsamples were analysed using a 10-4-10 second scheme. Twelve cycle periods were used in each case. Multiplication of the cumulative detector response for the hafnium photopeak by an overall correction factor was the method of choice for determining the live time - dead time correction.

Statistical analysis of the hafnium data set revealed that all the glasses in group E had hafnium levels that were not statistically discernible from one another. In addition to this finding, some heterogeneity in the distribution of hafnium in 2 of the 4 refractive index groups was noted. Further study of the glasses in group A was suggested. Also, the analysis of several subsamples in group E would be beneficial. The Repeat term did not make any statistically

discernible contribution to the discrimination of various glasses within the same refractive index group.

Overall, at the 1-mg increment level 33% of all pairwise comparisons between glasses possessing the same refractive index were distinguishable on the basis of their hafnium content when a 1% experimentwise error rate was used. This rose to 52% at the 5-mg increment level. No additional discrimination of the nineteen glasses was provided by hafnium at either increment level when compared with the results for Na, Al and Ca.

The panes produced by a given manufacturer were found to be homogeneous in hafnium. No statistically discernible difference, at the 1% level of significance, was found between the hafnium levels contained in the glass formulations of the two manufacturers. The %RSD values associated with hafnium levels in the AFG/Pittsburgh panes at the 1-mg increment level were 25.1 and 17.1 for 16 and 24 analyses; these values decreased to 16.8 and 14.7 for 5-mg subsamples. Comparison of the panes of glass which had a known origin to those glasses provided by the RCMP revealed that approximately 40% of the hafnium values in the RCMP samples were statistically discernible from the produced panes.

And finally, boron carbide powder was embedded in a polymethyl methacrylate matrix to act as a thermal neutron shield. This produced a neutron filter that was relatively independent of the operating temperature of the reactor. Although no new elements were discovered which might aid in the discrimination of flat glasses, a significant reduction in background levels compared to conventional INAA experiments further reinforced the notion that modern flat glass production is a well controlled process.

5.2.1 Suggestions For Future Research

In general, the results contained in this thesis for the discrimination of flat glass samples are very encouraging. The promising results from this small data set would certainly warrant a wider survey of the glasses normally encountered in forensic case work studies in Canada and the province of Alberta in particular. The fact that none of the glasses provided by the RCMP appear to have been produced by either of the two major Canadian flat glass manufacturers investigated in this study is a concern. In addition to this slightly wider survey, glass produced by Domglas Ltd. (Redcliff, Alberta) and Bogardus Wilson Ltd. (Calgary, Alberta - a large distributor carrying a number of glasses from different foreign manufacturers) would be of interest. Glasses known to be produced by the float process should be included in this survey and the ability to discriminate among these samples should be evaluated.

Further study of the A and E group glasses should be initiated to confirm the heterogeneous distribution of hafnium within these glasses that was suggested by this study. Specifically, it would be of interest to determine the number of subsamples needed to adequately determine a statistically meaningful result for the hafnium content of the glasses. As an extension of this study, a number of glasses should be studied using pseudo-cyclic INAA[97,110-112]. Briefly, the technique irradiates all the given samples in a stack prior to irradiating the samples for a second cycle period. The time between irradiations allows for a greater reduction in the background levels associated with a particular photopeak than in CINAA and thus enables improved detection limits for nuclides with half-lives less than 25 seconds. Use of this technique may help to uncover some additional elements for the discrimination of flat glasses. The pseudo-cyclic experiment should be

available in the near future at the University of Alberta SLOWPOKE-2 reactor facility.

Throughout the course of this study, the importance of the homogeneity of variance assumption has been stressed. Any future work concerned with unequal sample sizes should address this problem. A plot of the residuals, $(Y-Y_{est})$, where Y is the experimentally obtained value and Y_{est} the estimate of Y based on the particular statistical model employed, versus Y_{est} should not indicate any systematic widening or narrowing (i.e. it should be approximately constant) when the homogeneity of variance assumption is obeyed. Concern with this problem led to the introduction of Parker's H-index[113,114] which calculates the natural logarithm of the variance (i.e. a variance-stabilising transformation). Other transformations of note which may be of help when the data set violates this assumption are the $Y^{1/2}$ and Y^X functions[115,116]. The use of an approximate t-test is also possible but no apparent concensus has been reached on the best method[117,118].

While this preliminary assessment of neutron activation analysis for the discrimination of flat glasses has concerned itself with only comparative results (i.e. semi-quantitative analyses), in the future quantitative results would be more appropriate. Quantitative analyses would allow the establishment and compiling of a data base which would be of particular use in determining how frequently a particular flat glass may be encountered within the population of available glasses. References 119 to 126 should help with the proper establishment of the levels of various elements within flat glass samples. It should be stressed that the work in this study may be easily converted to concentrations of the various elements at some later date due to the high stability associated with the neutron flux of a SLOWPOKE-2 nuclear

reactor. Presently, one drawback to a quantitative approach is the lack of certified reference materials. To the author's knowledge no known glass reference materials have been certified for sample sizes as small as 100-μg, or even 1-mg for that matter, for the major and minor constituents of flat glass samples. Therefore, the values produced in various labs would have to be screened carefully.

The above suggestions have all been restricted to the discrimination of flat glass samples. As alluded to in the summary section of this chapter, the type or classification of a particular glass fragment is also of considerable interest. The elements which have been found to be particularly good for the classification of various glasses are magnesium and manganese[75,127,42]. Their levels in this study, however, have not been reported since spectral interference between the 844-keV (Mg) and 847-keV (Mn) photopeaks is well known. Consideration of the less intense 1014-keV (Mg) and 1811-keV (Mn) photopeaks has not been successful for the determination of these elements in the small sample sizes considered here. Future work should consider the deconvolution of these two photopeaks, since magnesium has been noted to be the best classifying element known to date for the separation of sheet, container and tableware glasses[75,42]. Deconvolution using Fourier Transform techniques[128,129] is suggested; microcomputer programs with this option are available[130-133].

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Appendix 1

This appendix contains two sections. The first section deals with the instrumental neutron activation analysis (INAA) experiments performed on 19 glass samples supplied by an RCMP forensic laboratory. Raw data for the analysis by INAA of panes produced by two major Canadian flat glass manufacturers appear in the second section. Both sections report the results for sodium, aluminum and calcium analyses as described in chapter 2.

A1.1 Raw Data For INAA Experiments Performed on Nineteen Glass Samples

Appearing in this section are results for the INAA experiments described in sections 2.2.2 to 2.2.5. Nineteen glass fragments provided by an RCMP forensic laboratory were analysed for sodium, aluminum and calcium. Contained in column A are subsample labels. The letters and numbers appearing to the left of the hyphen indicate a glass sample while the numbers on the right are a subsample designation. Column B contains the date of analysis for each subsample. Appearing in columns C to F are the raw counts obtained for Na-1 (1369-keV photopeak of sodium), Na-2 (2754-keV photopeak of sodium), Al and Ca while columns G to J are the background counts underlying the photopeaks. In column K, average counts for a pulser (pulser 1) in the absence of a glass subsample are listed. This value was determined by averaging the pulser counts obtained prior to and immediately following a day's experiments. Contained in column L (pulser 2) are the counts resulting when the same pulser was counted during the acquisition of a glass subsample spectrum. Columns M and N list the background counts

associated with the two pulser peaks. Clock times appear in column O and the live times were either 600 (100-mg subsamples) or 300 seconds (1-mg subsamples) in duration. All of the above values were taken directly from output produced by a spectral peak searching routine (PREP 10) supplied by Nuclear Data. Finally, appearing in column P are the subsample masses in milligrams. The uncertainty associated with every measurement is ± 0.0017 milligrams. Blank values appear at the end of each data set and are separated from the subsamples for a particular refractive index group by a dashed line. A blank line separates glasses with different refractive index values.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Sub-	Date	Raw	Counts			Bkgrd.	Counts			Plsr.	Plsr.	Bkgrd.	Bkgrd.	ClockTime	Mass
2	sample		Na-1	Na-2	Al	Ca	Na-1	Na-2	Al	Ca	Cnts. 1	Cnts. 2	Cnts. 1	Cnts. 2	(seconds)	(mg)
3	A1-3	Oct. 27/87	14167	7182	28551	558	2213	216	1221	76	21796	21423	0	132	315.6	0.9729
4		Nov. 3/87	14130	7047	27264	518	2179	366	1108	185	21783	21423	3	120	315.2	0.9729
5		Nov. 10/87	13996	7031	27331	523	1904	248	1075	210	21788	21403	0	108	315	0.9729
6	A1-4	Oct. 27/87	13578	6763	26600	598	2542	194	1030	32	21796	21436	0	83	314.8	0.9728
7		Nov. 3/87	14207	6965	27599	582	2108	355	903	66	21783	21440	3	81	315.2	0.9728
8		Nov. 10/87	13774	7059	27740	574	2135	223	1125	171	21788	21472	0	85	315.3	0.9728
9	A1-5	Nov. 19/87	14356	7201	27719	566	2198	270	927	181	21846	21424	0	94	315.6	0.9688
10		Nov. 5/87	14005	6996	27037	545	2228	182	1107	95	21792	21415	0	115	315.2	0.9688
11		Nov. 12/87	13695	6937	27094	513	2340	250	935	181	21771	21424	9	105	315.1	0.9688
12	A1-6	Oct. 29/87	14375	7234	27878	548	3341	220	918	55	21779	21416	1	85	315.5	0.975
13		Nov. 5/87	14079	7115	27842	567	2083	219	825	112	21792	21408	0	116	315.3	0.975
14		Nov. 19/87	13914	7055	26835	550	2076	171	968	162	21846	21494	0	147	315.2	0.975
15	A1-9	Oct. 27/87	7296	3671	5183	192	584	68	375	36	43591	43418	0	16	609	0.1014
16		Nov. 3/87	7870	3822	5171	198	756	168	285	50	43566	43424	6	44	609.2	0.1014
17		Nov. 10/87	7236	3733	5025	206	595	68	357	28	43575	43392	0	63	608.8	0.1014
18	A1-10	Oct. 27/87	7333	3610	5131	206	564	121	328	61	43591	43594	0	4	608.9	0.0957
19		Nov. 3/87	7324	3698	4798	195	1001	81	356	44	43566	43438	6	32	608.7	0.0957
20		Nov. 10/87	6802	3379	4761	166	759	126	204	0	43575	43450	0	50	608.2	0.0957
21	A1-11	Oct. 29/87	6465	3214	4765	197	680	9	615	8	43558	43401	2	22	608.5	0.0924
22		Nov. 5/87	6921	3370	4724	181	688	155	531	12	43583	43427	0	54	608.9	0.0924
23		Nov. 19/87	6464	3327	4877	190	642	310	270	9	43692	43521	0	27	608.5	0.0924
24	A1-12	Nov. 19/87	6740	3488	4843	163	732	110	252	21	43692	43542	0	26	608.5	0.0904
25		Nov. 5/87	7272	3561	4837	191	568	96	308	32	43583	43420	0	20	608.8	0.0904
26		Nov. 12/87	6617	3369	4661	171	798	109	394	18	43542	43440	18	31	608.2	0.0904
27	A2-3	Nov. 17/87	13691	6880	32139	509	2816	265	1012	154	21824	21432	2	109	316.4	0.9708

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
28		Nov. 3/87	14130	7077	33750	568	2748	308	1095	72	21783	21332	3	92	316.8	0.9708
29		Nov. 10/87	13280	6769	31402	525	2490	242	969	63	21788	21393	0	105	315.9	0.9708
30	A2-4	Oct. 27/87	14014	7048	33136	581	2882	220	1052	68	21796	21343	0	116	316.8	0.9745
31		Nov. 3/87	14118	7050	33031	541	2865	205	1350	55	21783	21960	3	7	316.4	0.9745
32		Nov. 10/87	13939	6613	32748	502	2457	394	1131	156	21788	21439	0	6	316.5	0.9745
33	A2-5	Oct. 29/87	14036	7123	32416	547	2460	207	969	60	21779	21324	1	79	316.4	0.9684
34		Nov. 5/87	14026	7241	33603	556	3335	247	1088	92	21792	21449	0	150	316.9	0.9684
35		Nov. 12/87	14106	6993	33028	511	2771	264	1090	77	21771	21342	9	128	316.5	0.9684
36	A2-6	Oct. 29/87	14253	7249	33741	560	2546	246	1026	150	21779	21472	1	77	316.8	0.975
37		Nov. 5/87	14145	7002	32391	543	2334	265	1271	88	21792	21443	0	77	316.6	0.975
38		Nov. 12/87	14400	7028	33394	551	2408	205	935	64	21771	21480	9	77	316.6	0.975
39	A2-9	Oct. 27/87	6533	3411	5738	174	710	71	436	68	43591	43434	0	26	608.6	0.0892
40		Nov. 3/87	6534	3222	5565	182	750	108	310	22	43566	43403	6	40	608.3	0.0892
41		Nov. 10/87	6361	3192	5446	166	550	95	308	40	43575	43420	0	54	608.2	0.0892
42	A2-10	Oct. 27/87	7565	3872	6330	228	599	176	309	24	43591	43398	0	44	609.3	0.1002
43		Nov. 3/87	7357	3757	6145	171	1358	178	457	116	43566	43364	6	40	609.1	0.1002
44		Nov. 10/87	7412	3810	6185	204	497	290	257	36	43575	43561	0	2	609	0.1002
45	A2-11	Oct. 29/87	7442	3719	5908	184	795	144	328	21	43558	43400	2	21	609.3	0.0968
46		Nov. 5/87	7478	3700	5937	215	623	121	552	4	43583	43412	0	23	609.4	0.0968
47		Nov. 19/87	7111	3711	5884	172	197	174	383	33	43692	43545	0	47	609.1	0.0968
48	A2-12	Oct. 29/87	7048	3621	5847	170	845	181	368	37	43558	43371	2	127	609.2	0.0955
49		Nov. 5/87	7226	3647	5976	223	796	114	340	20	43583	43422	0	26	609.3	0.0955
50		Nov. 19/87	6996	3449	5733	163	696	219	613	55	43692	43539	0	17	609.1	0.0955
51	A3-3	Nov. 17/87	14168	6981	29266	566	2351	205	1044	68	21824	21505	2	73	316	0.9723
52		Nov. 3/87	13826	7044	28582	540	3647	290	1065	55	21783	21398	3	123	315.6	0.9723
53		Nov. 10/87	14141	7153	29349	548	2534	259	888	161	21788	21473	0	64	315.8	0.9723
54	A3-4	Oct. 27/87	13724	7005	28313	597	3024	212	1129	44	21796	21411	0	102	315.3	0.9691

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
55		Nov. 3/87	14128	7134	28625	556	2727	195	1188	165	21783	21399	3.	77	315.6	0.9691
56		Nov. 10/87	13788	7115	29008	524	2207	266	966	145	21788	21430	0	99	315.7	0.9691
57	A3-5	Oct. 29/87	14172	7030	28560	572	2224	226	1097	50	21779	21396	1	68	315.6	0.9697
58		Nov. 5/87	14145	6983	29024	539	2264	230	1845	182	21792	21447	0	88	315.7	0.9697
59		Nov. 12/87	13742	6891	28766	487	2170	162	907	167	21771	21457	9	92	315.5	0.9697
60	A3-6	Oct. 29/87	14318	7136	28535	572	2250	294	1175	52	21779	21364	1	72	315.5	0.9707
61		Nov. 5/87	13985	7093	28909	545	2272	268	837	44	21792	21467	0	94	315.5	0.9707
62		Nov. 19/87	13828	6908	29077	544	738	204	844	46	21846	21425	0	98	315.7	0.9707
63	A3-9	Nov. 17/87	6769	3301	5088	162	530	77	486	34	43649	43542	3	66	608.5	0.094
64		Nov. 3/87	6856	3490	5320	191	637	150	248	48	43566	43384	6	32	609	0.094
65		Nov. 10/87	6806	3480	5188	179	727	140	266	13	43575	43392	0	32	608.6	0.094
66	A3-10	Oct. 27/87	7208	3614	5391	196	855	63	302	46	43591	43467	0	6	609	0.0969
67		Nov. 3/87	7703	3834	5389	216	588	105	276	13	43566	43392	6	43	609.2	0.0969
68		Nov. 10/87	7361	3649	5367	204	704	157	400	20	43575	43437	0	26	608.9	0.0969
69	A3-11	Oct. 29/87	7140	3664	5071	203	718	77	353	7	43558	43373	2	41	609	0.0944
70		Nov. 5/87	6960	3529	5087	184	518	90	279	165	43583	43013	0	5	608.6	0.0944
71		Nov. 19/87	6840	3492	5094	203	1269	168	235	33	43692	43229	0	3	608.7	0.0944
72	A3-12	Oct. 29/87	6432	3219	4764	192	695	104	233	23	43558	43414	2	38	608.4	0.0902
73		Nov. 5/87	6856	3531	4877	196	599	70	378	6	43583	43402	0	32	608.7	0.0902
74		Nov. 12/87	6443	3177	4664	175	616	98	328	25	43542	43439	18	13	608.2	0.0902
75	A5-3	Oct. 27/87	13629	6879	25450	595	2410	278	876	102	21796	21515	0	69	314.6	0.9743
76		Nov. 3/87	13960	6907	24953	582	1849	324	1018	40	21783	21463	3	77	314.4	0.9743
77		Nov. 10/87	13490	6691	25033	579	2264	476	982	30	21788	21443	0	85	314.5	0.9743
78	A5-4	Oct. 27/87	13291	6681	24748	543	2120	263	856	121	21796	21603	0	14	314.2	0.9712
79		Nov. 3/87	13945	6949	25629	645	2641	204	979	37	21783	21295	3	11	314.7	0.9712
80		Nov. 10/87	13734	6842	25153	610	2189	264	915	120	21788	21483	0	94	314.4	0.9712
81	A5-5	Oct. 29/87	13673	6860	25265	602	1991	203	910	189	21779	21427	1	68	314.5	0.9751

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
82		Nov. 5/87	13756	6864	25396	590	2009	364	936	45	21792	21390	0	94	314.6	0.9751
83		Nov. 19/87	13776	6860	25435	610	2208	238	905	50	21846	21494	0	56	314.7	0.9751
84	A5-6	Oct. 29/87	13616	6808	25146	603	2089	225	919	48	21779	21407	1	49	314.4	0.976
85		Nov. 5/87	13864	6889	25406	543	2977	285	1156	196	21792	21366	0	13	314.7	0.976
86		Nov. 12/87	13632	6805	25801	595	1984	199	820	44	21771	21464	9	68	314.5	0.976
87	A5-9	Oct. 27/87	6361	3120	4153	181	574	100	234	15	43591	43416	0	20	608.3	0.089
88		Nov. 3/87	6560	3351	3943	199	551	95	481	14	43566	43455	6	43	608.4	0.089
89		Nov. 10/87	6256	3263	3966	168	516	98	320	32	43575	43322	0	4	608.2	0.089
90	A5-10	Nov. 17/87	6694	3392	4443	199	578	105	310	20	43649	43544	3	36	608.6	0.0963
91		Nov. 3/87	7470	3609	4806	202	497	122	437	18	43566	43421	6	15	609.3	0.0963
92		Nov. 10/87	6801	3429	4408	183	670	145	310	116	43575	43440	0	20	608.6	0.0963
93	A5-11	Nov. 19/87	7144	3646	4672	208	1356	85	315	47	43692	43515	0	18	609	0.0995
94		Nov. 5/87	7109	3583	4559	216	595	25	409	3	43583	43444	0	41	609	0.0995
95		Nov. 12/87	7274	3515	4746	211	662	110	370	26	43542	43402	18	36	608.8	0.0995
96	A5-12	Oct. 29/87	7440	3608	5258	232	770	108	296	2	43558	43409	2	32	608.8	0.0995
97		Nov. 5/87	7430	3642	5038	199	808	206	323	48	43583	43462	0	35	608.8	0.0995
98		Nov. 19/87	7373	3760	5006	230	815	130	353	25	43692	43477	0	30	608.9	0.0995
99	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
100	Bl-R	Oct. 27/87	120	54	289	0	32	0	38	0	21796	21783	0	0	301.8	
101		Nov. 3/87	60	35	292	0	149	0	14	0	21783	21758	3	0	301.8	
102		Nov. 10/87	21	0	322	0	9	0	12	0	21788	21769	0	0	301.8	
103	Bl-T	Oct. 29/87	114	28	156	0	14	0	54	0	21779	21756	1	3	301.8	
104		Nov. 5/87	161	105	220	0	145	5	32	0	21792	21779	0	0	301.9	
105		Nov. 12/87	175	72	210	0	9	0	58	0	21771	21750	9	2	301.8	
106	Bl-S	Oct. 27/87	76	26	501	0	36	0	32	0	43591	43545	0	0	604.6	
107		Nov. 3/87	291	170	540	0	83	4	102	0	43566	43539	6	0	604.5	
108		Nov. 10/87	105	60	468	0	84	0	80	0	43575	43559	0	0	604.3	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
109	Bl-U	Oct. 29/87	503	246	426	0	114	12	78	0	43558	43472	2	15	604.9	
110		Nov. 5/87	412	212	461	3	157	5	95	0	43583	43524	0	4	604.8	
111		Nov. 12/87	233	102	399	0	182	33	77	0	43542	43452	18	10	604.6	
112																
113	B1-3	Aug. 13/87	13961	6896	37189	734	4065	284	1067	48	21574	21140	1	86	317.2	0.958
114		Jul. 28/87	13760	6954	36927	691	2401	210	1017	85	21567	21140	0	94	316.9	0.958
115		Aug. 4/87	13875	6985	37384	737	2816	318	1139	55	21558	21147	2	104	317.4	0.958
116	B1-4	Jul. 21/87	14093	7125	37793	784	2604	234	1323	43	21607	21057	0	132	317.6	0.9635
117		Jul. 28/87	13291	6731	35914	684	2457	331	1206	58	21567	21144	0	86	316.9	0.9635
118		Aug. 4/87	13425	6828	36325	684	3277	235	1232	30	21558	21122	2	100	316.9	0.9635
119	B1-5	Jul. 23/87	14087	7068	38138	752	2768	305	1238	63	21604	21183	1	121	317.3	0.9713
120		Jul. 30/87	14030	7089	37635	713	2730	212	1416	69	21556	21175	0	108	317.4	0.9713
121		Aug. 6/87	13923	6915	37450	708	2604	234	1293	60	21572	21086	0	131	317.3	0.9713
122	B1-6	Jul. 23/87	13758	6677	37459	738	2622	297	1019	40	21604	21198	1	86	317.2	0.9622
123		Jul. 30/87	14009	6827	38240	736	2769	225	1205	181	21556	21188	0	105	317.4	0.9622
124		Aug. 6/87	13490	6797	36401	689	2940	268	1139	72	21572	21176	0	86	317.1	0.9622
125	B1-9	Aug. 13/87	6816	3411	6551	237	649	120	308	20	43148	42945	2	38	608.9	0.0928
126		Jul. 28/87	6595	3446	6472	203	705	175	308	83	43134	42988	0	30	609	0.0928
127		Aug. 4/87	6530	3234	6752	203	1067	160	296	44	43115	42952	4	53	608.9	0.0928
128	B1-10	Jul. 21/87	6641	3264	6285	222	873	92	324	28	43214	43026	0	28	608.8	0.0925
129		Jul. 28/87	6828	3423	6481	235	1007	90	353	72	43134	42888	0	53	608.9	0.0925
130		Aug. 4/87	6747	3377	6369	221	566	116	292	23	43115	42921	4	34	608.7	0.0925
131	B1-11	Jul. 23/87	7261	3513	6766	247	638	70	337	73	43207	43070	2	49	609.1	0.0965
132		Jul. 30/87	7094	3543	6536	248	668	59	420	33	43112	42958	0	15	608.9	0.0965
133		Aug. 6/87	7139	3641	6637	291	1018	131	371	20	43144	42992	0	29	609	0.0965
134	B1-12	Jul. 23/87	6907	3477	6451	229	606	90	394	17	43207	42972	2	36	609	0.093
135		Jul. 30/87	6962	3367	6563	250	936	104	315	36	43112	42927	0	33	608.9	0.093

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
136		Aug. 6/87	6852	3389	6444	230	664	106	380	14	43144	43023	0	36	608.8	0.093
137	B2-3	Jul. 21/87	14925	7512	7498	597	1029	200	560	50	21607	21448	0	36	310.4	0.9564
138		Jul. 28/87	14288	7137	7682	566	1165	230	485	98	21567	21354	0	70	310.1	0.9564
139		Aug. 4/87	14520	7391	7600	562	1690	70	561	57	21558	21351	2	45	310.3	0.9564
140	B2-4	Jul. 21/87	14853	7251	7757	566	956	238	484	156	21607	21394	0	95	310.4	0.967
141		Jul. 28/87	14439	7281	7570	589	1192	157	533	173	21567	21347	0	59	310.1	0.967
142		Aug. 4/87	14945	7361	7846	614	868	69	574	130	21558	21302	2	85	310.3	0.967
143	B2-5	Jul. 23/87	14681	7347	7657	593	1060	180	1053	27	21604	21358	1	100	310.4	0.9703
144		Jul. 30/87	14725	7430	7821	592	847	245	561	98	21556	21347	0	42	310.3	0.9703
145		Aug. 6/87	14969	7571	8447	592	994	168	513	180	21572	21387	0	32	310.5	0.9703
146	B2-6	Aug. 13/87	14561	7348	7712	542	1076	203	660	182	21574	21330	1	96	310.3	0.9609
147		Jul. 30/87	14818	7374	8188	565	1197	158	612	109	21556	21305	0	58	310.4	0.9609
148		Aug. 6/87	14407	7313	7527	549	1124	253	548	50	21572	21316	0	38	310.2	0.9609
149	B2-9	Jul. 21/87	6712	3335	1606	149	396	68	242	30	43214	43126	0	35	607.7	0.0894
150		Jul. 28/87	6738	3546	1703	176	412	81	215	15	43134	43039	0	18	607.7	0.0894
151		Aug. 4/87	6838	3433	1634	166	357	119	214	34	43115	42946	4	25	607.6	0.0894
152	B2-10	Jul. 21/87	7206	3697	1799	222	472	149	385	15	43214	43047	0	18	608	0.0961
153		Jul. 28/87	7172	3577	1770	211	475	60	268	60	43134	42990	0	19	607.8	0.0961
154		Aug. 13/87	7453	3632	1844	189	522	128	214	21	43148	42987	2	23	607.9	0.0961
155	B2-11	Jul. 23/87	7747	3868	1613	197	475	99	286	52	43207	43016	2	26	608.2	0.0987
156		Jul. 30/87	7603	3745	1627	190	343	136	300	95	43112	42953	0	28	608	0.0987
157		Aug. 6/87	7491	3859	1626	203	713	116	373	14	43144	43058	0	25	608	0.0987
158	B2-12	Jul. 23/87	6870	3329	1575	199	467	124	195	19	43207	43059	2	44	607.7	0.0886
159		Jul. 30/87	6738	3414	1656	188	360	105	259	11	43112	42975	0	18	607.8	0.0886
160		Aug. 13/87	7049	3630	1716	200	495	98	228	16	43148	42964	2	53	607.9	0.0886
161	B3-3	Aug. 13/87	14628	7460	8536	567	1202	250	672	81	21574	21347	1	88	310.6	0.9748
162		Jul. 28/87	14603	7327	8377	538	1348	253	564	91	21567	21339	0	63	310.5	0.9748

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
163		Aug. 4/87	14563	7206	8265	547	1031	230	591	72	21558	21353	2	71	310.5	0.9748
164	B3-4	Jul. 21/87	14613	7264	8261	566	893	263	561	62	21607	21430	0	42	310.4	0.9632
165		Jul. 28/87	13999	7227	7430	569	1233	248	584	104	21567	21340	0	63	310.1	0.9632
166		Aug. 4/87	13861	6805	7886	599	1079	336	603	123	21558	21334	2	62	310	0.9632
167	B3-5	Jul. 23/87	14008	7217	7962	561	1103	208	469	130	21604	21400	1	42	310.2	0.9713
168		Jul. 30/87	14509	7390	8145	595	959	242	1134	30	21556	21306	0	88	310.4	0.9713
169		Aug. 6/87	14574	7159	8008	601	1118	240	473	15	21572	21364	0	90	310.3	0.9713
170	B3-6	Jul. 23/87	14206	6980	8487	524	1075	490	775	71	21604	21382	1	55	310.4	0.9588
171		Jul. 30/87	14573	7365	8890	585	1075	166	476	38	21556	21334	0	65	310.5	0.9588
172		Aug. 6/87	13989	7122	7943	540	1152	213	580	176	21572	21377	0	124	310.1	0.9588
173	B3-9	Jul. 21/87	6561	3386	1527	202	294	120	184	26	43214	43081	0	15	607.6	0.0885
174		Jul. 28/87	6447	3307	1438	166	400	119	272	44	43134	43031	0	16	607.5	0.0885
175		Aug. 4/87	6711	3357	1452	192	540	14	259	58	43115	42945	4	28	607.5	0.0885
176	B3-10	Jul. 21/87	7241	3738	1643	195	360	86	252	41	43214	43069	0	28	608	0.0962
177		Jul. 28/87	7135	3763	1642	200	432	126	260	30	43134	43024	0	11	607.9	0.0962
178		Aug. 13/87	7342	3647	1712	203	386	161	400	39	43148	43049	2	26	607.9	0.0962
179	B3-11	Aug. 13/87	7496	3755	1650	192	412	71	301	73	43148	42782	2	4	608	0.0983
180		Jul. 30/87	7444	3739	1615	221	495	81	350	45	43112	42941	0	25	607.9	0.0983
181		Nov. 17/87	7641	3914	1764	219	1203	132	293	19	43649	43523	3	25	608.2	0.0983
182	B3-12	Jul. 23/87	7530	3733	1500	163	364	81	192	41	43207	43000	2	86	608	0.096
183		Jul. 30/87	7675	3871	1623	204	396	169	306	37	43112	42942	0	33	608.1	0.096
184		Aug. 6/87	7156	3669	1676	164	534	88	247	77	43144	42980	0	48	607.7	0.096
185	B4-3	Jul. 21/87	14376	7318	7687	614	1131	290	770	59	21607	21381	0	68	310.3	0.9634
186		Jul. 28/87	14368	7115	7822	572	1165	183	523	63	21567	21324	0	49	310.2	0.9634
187		Aug. 4/87	14153	7130	7466	549	1025	261	655	47	21558	21359	2	42	310.1	0.9634
188	B4-4	Jul. 21/87	14852	7363	7608	590	964	252	574	217	21607	21340	0	68	310.4	0.9587
189		Jul. 28/87	14061	7156	7414	605	1113	226	556	68	21567	21380	0	60	310.1	0.9587

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
190		Aug. 4/87	14029	7184	7251	558	1264	162	548	38	21558	21359	2	34	309.9	0.9587
191	B4-5	Jul. 23/87	14613	7306	8244	628	1096	208	480	114	21604	21375	1	71	310.4	0.969
192		Jul. 30/87	14741	7252	7507	621	1052	285	476	41	21556	21271	0	80	310.2	0.969
193		Aug. 6/87	14168	7181	7265	590	1121	196	504	60	21572	21365	0	105	310	0.969
194	B4-6	Aug. 13/87	14103	7187	7454	567	1016	181	648	77	21574	21297	1	138	310.1	0.9639
195		Jul. 30/87	14463	7177	7809	573	1334	187	454	181	21556	21334	0	67	310.3	0.9639
196		Aug. 6/87	14272	7077	7589	573	1124	290	649	51	21572	21392	0	72	310.2	0.9639
197	B4-9	Jul. 21/87	7063	3479	1557	195	384	104	242	13	43214	43103	0	19	607.7	0.094
198		Jul. 28/87	6991	3473	1570	183	386	114	266	105	43134	43006	0	32	607.5	0.094
199		Aug. 4/87	6892	3605	1534	193	489	77	260	60	43115	43015	4	18	607.6	0.094
200	B4-10	Jul. 21/87	6782	3400	1617	162	356	126	252	30	43214	43047	0	25	607.6	0.0867
201		Jul. 28/87	6561	3363	1546	215	412	100	231	4	43134	43033	0	19	607.6	0.0867
202		Aug. 4/87	6610	3371	1543	163	552	95	260	21	43115	42961	4	66	607.5	0.0867
203	B4-11	Jul. 23/87	7116	3548	1783	201	340	81	296	22	43207	43032	2	34	608	0.0953
204		Jul. 30/87	7264	3620	1918	217	384	108	276	16	43112	42991	0	22	608	0.0953
205		Aug. 6/87	7139	3504	1834	196	494	110	240	18	43144	43008	0	45	607.9	0.0953
206	B4-12	Jul. 23/87	6912	3443	1456	150	400	81	273	99	43207	43064	2	28	607.6	0.0902
207		Jul. 30/87	6776	3446	1567	166	683	95	150	18	43112	43011	0	21	607.6	0.0902
208		Aug. 6/87	6776	3402	1325	190	260	86	186	39	43144	43036	0	24	607.5	0.0902
209	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
210	Bl-N	Jul. 21/87	0	14	555	0	0	0	26	0	21607	21592	0	0	301.8	
211		Aug. 13/87	79	48	450	0	72	0	11	0	21574	21545	1	3	301.8	
212		Aug. 4/87	42	28	455	0	123	0	8	0	21558	21532	2	7	301.8	
213	Bl-P	Jul. 23/87	62	11	158	0	27	0	15	0	21604	21586	1	0	301.7	
214		Aug. 13/87	45	24	181	0	56	0	14	0	21574	21557	1	4	301.7	
215		Aug. 6/87	66	28	191	0	9	0	14	0	21572	21554	0	4	301.7	
216	Bl-O	Jul. 21/87	158	62	431	0	45	15	43	0	43214	43161	0	4	604.5	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
217		Jul. 28/87	87	53	406	7	111	0	34	0	43134	43088	0	4	604.4	
218		Aug. 4/87	194	110	407	0	39	0	68	0	43115	43053	4	15	604.4	
219	Bl-Q	Jul. 23/87	126	37	412	0	176	10	34	0	43207	43128	2	4	604.3	
220		Jul. 30/87	250	103	321	0	137	0	74	0	43112	43045	0	7	604.3	
221		Aug. 6/87	195	88	316	0	55	0	56	0	43144	43094	0	0	604.3	
222																
223	C1-4	Mar. 3/87	12611	6384	31425	529	2648	180	932	81	21918	21448	0	6	315.7	0.9426
224		Mar. 10/87	12669	6355	31804	535	2943	225	900	72	21929	21569	2	68	315.7	0.9426
225		Mar. 17/87	12637	6236	31724	513	2438	200	1002	63	21917	21564	3	44	315.7	0.9426
226	C1-5	Mar. 3/87	12375	6228	31397	532	2490	176	948	84	21918	21547	0	88	315.5	0.9282
227		Mar. 10/87	12593	6191	31187	518	2316	200	1045	122	21929	21611	2	116	315.4	0.9282
228		Mar. 17/87	12423	6107	31363	482	3249	275	1092	173	21917	21579	3	65	315.6	0.9282
229	C1-6	Mar. 5/87	11922	6137	30102	508	2714	200	959	83	21920	21517	0	79	315.1	0.9161
230		Mar. 12/87	12504	6237	30974	506	2456	257	905	142	21934	21521	0	169	315.4	0.9161
231		Mar. 19/87	12510	6260	30801	582	2563	279	1036	33	21904	21505	0	100	315.6	0.9161
232	C1-8	Mar. 5/87	12419	6252	31051	534	2528	264	979	6	21920	21491	0	77	315.5	0.9344
233		Mar. 12/87	12844	6300	32409	628	2411	230	1040	81	21934	21532	0	64	316	0.9344
234		Mar. 19/87	12214	6313	31046	493	2758	230	1097	57	21904	21522	0	77	315.5	0.9344
235	C1-9	Mar. 3/87	6791	3307	5720	195	584	203	441	26	43836	43697	0	23	608.7	0.0996
236		Mar. 10/87	6669	3332	5816	156	725	216	373	109	43858	43690	4	11	608.7	0.0996
237		Mar. 17/87	6721	3481	5591	196	553	81	425	5	43834	43678	6	16	608.6	0.0996
238	C1-11	Mar. 3/87	6551	3369	5876	203	774	128	252	10	43836	43653	0	35	608.8	0.0931
239		Mar. 10/87	6705	3423	5761	194	560	72	667	21	43858	43643	4	29	608.7	0.0931
240		Mar. 17/87	6492	3312	5907	192	650	105	284	24	43834	43662	6	26	608.5	0.0931
241	C1-12	Mar. 5/87	6509	3137	5561	198	700	104	208	26	43840	43655	0	24	608.6	0.0881
242		Mar. 12/87	6281	3128	5688	183	613	95	326	19	43867	43638	0	42	608.6	0.0881
243		Mar. 19/87	6105	3056	5601	194	888	132	518	13	43807	43617	0	23	608.5	0.0881

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
244	C1-13	Mar. 5/87	6013	3020	5379	187	468	75	391	27	43840	43662	0	22	608.5	0.0899
245		Mar. 12/87	6101	3224	5484	190	1008	85	300	5	43867	43657	0	28	608.5	0.0899
246		Mar. 19/87	6079	3082	5184	144	732	45	347	35	43807	43649	0	39	608.4	0.0899
247	C2-4	Mar. 3/87	12610	6354	31655	555	2899	230	1225	30	21918	21611	0	59	315.6	0.9328
248		Mar. 10/87	12735	6048	31500	515	2244	270	1045	51	21929	21589	2	66	315.5	0.9328
249		Mar. 17/87	12194	6207	31211	560	4194	246	922	81	21917	21637	3	32	315.4	0.9328
250	C2-5	Mar. 5/87	12340	6420	31212	553	2158	203	882	28	21920	21564	0	80	315.7	0.9151
251		Mar. 12/87	12702	6395	31348	496	2588	297	1325	74	21934	21498	0	72	315.6	0.9151
252		Mar. 19/87	12289	6050	30656	488	2404	178	1055	56	21904	21454	0	98	315.3	0.9151
253	C2-6	Mar. 3/87	12552	6386	31800	538	2351	184	1029	47	21918	21575	0	56	315.6	0.9421
254		Mar. 10/87	12220	6250	31121	546	2566	198	1624	41	21929	21521	2	85	315.4	0.9421
255		Mar. 17/87	12915	6433	32379	508	2568	311	1002	86	21917	21539	3	104	316	0.9421
256	C2-7	Mar. 5/87	13104	6461	32373	530	2250	196	910	135	21920	21517	0	80	316	0.9501
257		Mar. 12/87	13278	6587	32606	567	3386	189	1128	98	21934	21528	0	83	316.1	0.9501
258		Mar. 19/87	12731	6533	31655	578	3755	266	1053	55	21904	21533	0	71	316	0.9501
259	C2-9	Mar. 3/87	7717	3768	6425	251	704	110	414	27	43836	43674	0	28	609.4	0.1064
260		Mar. 10/87	7166	3627	6272	203	630	86	327	35	43858	43659	4	20	609.1	0.1064
261		Mar. 17/87	7126	3491	6253	180	585	165	390	74	43834	43677	6	41	609.1	0.1064
262	C2-11	Mar. 3/87	6029	3044	5306	179	525	25	330	35	43836	43689	0	23	608.3	0.09
263		Mar. 10/87	6006	2926	5303	177	581	128	325	34	43858	43705	4	30	608.3	0.09
264		Mar. 17/87	5948	2991	5295	170	740	81	293	26	43834	43658	6	28	608.3	0.09
265	C2-12	Mar. 5/87	6704	3469	5635	185	744	132	315	50	43840	43657	0	41	609	0.0966
266		Mar. 12/87	6544	3314	5923	185	651	92	488	13	43867	43640	0	35	609.1	0.0966
267		Mar. 19/87	6684	3287	6018	189	680	116	355	15	43807	43665	0	30	609.1	0.0966
268	C2-14	Mar. 5/87	6558	3262	5859	162	585	114	311	63	43840	43663	0	34	608.9	0.0976
269		Mar. 12/87	6787	3245	5996	189	627	114	326	15	43867	43702	0	19	608.9	0.0976
270		Mar. 19/87	6530	3324	5784	180	648	120	327	54	43807	43632	0	3	608.8	0.0976

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
271	C3-3	Mar. 5/87	13209	6726	27717	562	2930	236	914	40	21920	21553	0	53	314.8	0.9268
272		Mar. 12/87	13400	6798	28666	529	2030	273	972	62	21934	21526	0	75	315.1	0.9268
273		Mar. 19/87	13037	6753	28014	529	2790	363	969	108	21904	21555	0	51	315	0.9268
274	C3-4	Mar. 3/87	13436	6757	28187	525	2250	176	891	40	21918	21630	0	53	314.9	0.9303
275		Mar. 10/87	13446	6783	28377	498	2104	242	893	70	21929	21576	2	101	314.9	0.9303
276		Mar. 17/87	13648	6774	28570	527	2296	245	1029	89	21917	21623	3	8	315.1	0.9303
277	C3-5	Mar. 3/87	13076	6731	27706	518	2096	239	803	54	21918	21554	0	56	314.7	0.9019
278		Mar. 10/87	12966	6530	27235	460	2120	187	778	188	21929	21611	2	41	314.4	0.9019
279		Mar. 17/87	12476	6336	26647	567	2025	166	941	32	21917	21568	3	64	314	0.9019
280	C3-7	Mar. 5/87	13388	6880	28297	525	2160	225	1110	111	21920	21619	0	99	314.9	0.929
281		Mar. 12/87	13628	6725	28332	525	2364	205	897	55	21934	21620	0	45	314.9	0.929
282		Mar. 19/87	13798	6770	29163	588	2261	330	1084	83	21904	21472	0	119	315.4	0.929
283	C3-10	Mar. 3/87	7417	3640	5306	213	740	150	370	43	43836	43681	0	52	608.6	0.1008
284		Mar. 10/87	7670	3726	5469	216	672	95	333	74	43858	43628	4	26	608.8	0.1008
285		Mar. 17/87	7352	3823	5483	202	756	63	375	16	43834	43697	6	14	608.7	0.1008
286	C3-11	Mar. 3/87	6503	3141	4727	193	515	168	289	36	43836	43705	0	39	608.4	0.0908
287		Mar. 10/87	6857	3616	5049	183	684	70	340	59	43858	43745	4	39	608.5	0.0908
288		Mar. 17/87	6631	3315	4980	170	830	115	275	32	43834	43692	6	32	608.3	0.0908
289	C3-13	Mar. 5/87	6829	3349	4996	173	504	149	336	28	43840	43728	0	21	608.5	0.0934
290		Mar. 12/87	6707	3370	5040	153	172	100	259	24	43867	43726	0	13	608.4	0.0934
291		Mar. 19/87	6791	3524	4929	194	877	115	370	5	43807	43621	0	52	608.5	0.0934
292	C3-14	Mar. 5/87	6832	3362	4832	200	667	126	304	11	43840	43664	0	23	608.5	0.0941
293		Mar. 12/87	6679	3470	5045	185	581	98	268	42	43867	43670	0	21	608.3	0.0941
294		Mar. 19/87	6617	3330	4852	184	656	175	336	25	43807	43656	0	24	608.4	0.0941
295	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
296	B1-A	Mar. 3/87	32	22	1	0	41	0	1	0	21918	21888	0	0	301.8	
297		Mar. 10/87	0	0	216	0	0	0	24	0	21929	21909	2	0	301.8	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
298		Mar. 17/87	25	0	190	0	34	0	4	0	21917	21899	3	4	301.7	
299	Bl-D	Mar. 5/87	137	61	244	0	18	0	24	0	21920	21885	0	0	302	
300		Mar. 12/87	8	4	239	0	44	0	14	0	21934	21908	0	3	301.9	
301		Mar. 19/87	79	26	302	0	90	0	7	0	21904	21865	0	0	301.9	
302	Bl-B	Mar. 3/87	237	132	353	0	198	4	53	0	43836	43756	0	7	604.4	
303		Mar. 10/87	121	71	461	0	243	4	63	0	43858	43787	4	11	604.4	
304		Mar. 17/87	156	75	378	0	75	19	55	0	43834	43766	6	13	604.3	
305	Bl-C	Mar. 5/87	115	57	395	0	91	4	64	0	43840	43791	0	8	604.4	
306		Mar.12/87	146	48	459	0	38	0	25	0	43867	43761	0	7	604.3	
307		Mar. 19/87	44	26	516	0	76	13	56	0	43807	43780	0	7	604.4	
308																
309	D1-3	Jun. 30/87	14639	7323	26047	496	2817	212	922	48	21655	21303	1	52	315.1	0.9734
310		Nov. 17/87	15028	7448	26142	562	2188	264	1016	56	21824	21505	2	79	315.5	0.9734
311		Jul. 14/87	15038	7729	26717	549	2741	436	918	43	21640	21246	0	52	315.4	0.9734
312	D1-4	Jun. 30/87	14805	7330	25992	496	2208	233	825	26	21655	21319	1	71	315.2	0.9587
313		Jul. 7/87	14713	7314	25821	546	2589	242	996	117	21673	21350	1	104	315.2	0.9587
314		Jul. 14/87	14502	7373	26475	521	2448	300	1045	51	21640	21188	0	128	315.3	0.9587
315	D1-5	Jul. 2/87	14890	7451	26978	542	2260	176	884	30	21651	21304	0	67	315.3	0.968
316		Jul. 9/87	14935	7426	26266	561	2393	305	965	40	21624	21238	0	79	315.2	0.968
317		Jul. 16/87	14576	7403	25758	545	2079	221	1008	71	21640	21287	1	64	315.1	0.968
318	D1-6	Jul. 2/87	15023	7476	26961	531	2750	355	744	36	21651	21336	0	79	314.5	0.969
319		Nov. 17/87	15302	7645	27017	541	2340	272	922	45	21824	21433	2	81	316.1	0.969
320		Jul. 16/87	14994	7486	26329	569	1939	253	1344	96	21640	21237	1	75	315.3	0.969
321	D1-9	Jun. 30/87	7570	3742	4847	182	684	115	324	29	43310	43167	2	12	608.9	0.0969
322		Jul. 7/87	7317	3787	4709	174	634	68	328	23	43346	43182	2	26	608.8	0.0969
323		Jul. 14/87	7782	3899	4943	224	588	89	337	56	43280	43063	0	49	609	0.0969
324	D1-10	Jun. 30/87	6669	3233	4218	154	496	113	380	67	43310	43187	2	14	608.3	0.0908

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
325		Jul. 7/87	6492	3336	4507	151	592	89	347	30	43346	43239	2	15	608.4	0.0908
326		Jul. 14/87	6981	3425	4472	155	800	77	236	55	43280	43092	0	38	608.5	0.0908
327	D1-11	Jul. 2/87	7216	3508	4550	173	536	71	268	26	43302	43125	0	45	608.6	0.0923
328		Jul. 9/87	7462	3663	4464	164	506	108	324	29	43248	43091	0	35	608.7	0.0923
329		Nov. 17/87	7424	3857	4616	189	616	96	316	32	43649	43530	3	21	608.9	0.0923
330	D1-12	Jul. 2/87	6768	3482	4326	148	741	111	293	56	43302	43116	0	33	608.6	0.0904
331		Jul. 9/87	6832	3460	4336	153	688	95	308	70	43248	43064	0	26	608.5	0.0904
332		Jul. 16/87	7097	3394	4438	176	496	76	247	14	43280	43136	2	34	608.5	0.0904
333	D2-3	Jun. 30/87	13733	6980	27582	555	3681	221	970	45	21655	21307	1	48	315.1	0.9804
334		Jul. 7/87	13765	6861	27887	578	2209	194	799	34	21673	21312	1	67	315.1	0.9804
335		Jul. 14/87	13658	6804	26912	516	2084	314	927	43	21640	21337	0	94	314.8	0.9804
336	D2-4	Jun. 30/87	13605	6790	27780	556	2219	338	841	81	21655	21344	1	71	315	0.9772
337		Jul. 7/87	13889	7087	28165	596	2228	254	1181	81	21673	21346	1	88	315.2	0.9772
338		Jul. 14/87	13726	7011	28137	566	3388	268	1069	163	21640	21299	0	116	315.2	0.9772
339	D2-5	Jul. 2/87	13428	6749	27261	590	2031	228	972	53	21651	21307	0	100	314.9	0.9573
340		Jul. 9/87	13708	6797	27346	610	3050	238	945	36	21624	21255	0	56	315	0.9573
341		Jul. 16/87	13540	6784	27951	566	2352	345	824	60	21640	21248	1	94	315.1	0.9573
342	D2-6	Jul. 2/87	13602	6763	26966	556	2063	250	974	140	21651	21323	0	84	314.8	0.9611
343		Jul. 9/87	13762	6951	27496	492	2580	189	825	154	21624	21263	0	140	315	0.9611
344		Jul. 16/87	13422	6861	27055	525	1778	171	765	68	21640	21295	1	40	314.7	0.9611
345	D2-9	Jun. 30/87	6332	3174	4529	160	501	102	365	29	43310	43101	2	36	608.3	0.0925
346		Jul. 7/87	6663	3148	4761	183	760	136	385	19	43346	43206	2	20	608.6	0.0925
347		Jul. 14/87	6618	3373	4815	149	512	55	268	26	43280	43113	0	46	608.6	0.0925
348	D2-10	Jun. 30/87	6094	3143	4413	154	490	68	840	91	43310	43172	2	42	608.4	0.0916
349		Jul. 7/87	6431	3266	4561	206	595	90	268	15	43346	43203	2	30	608.4	0.0916
350		Jul. 14/87	6765	3355	4746	193	604	37	314	47	43280	43132	0	35	608.6	0.0916
351	D2-11	Jul. 2/87	6985	3479	5175	196	551	150	268	27	43302	43180	0	28	608.8	0.093

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
352		Jul. 9/87	6889	3449	5035	198	655	154	355	16	43248	43083	0	44	608.7	0.093
353		Jul. 16/87	7057	3405	4873	163	608	132	308	26	43280	43117	2	35	608.6	0.093
354	D2-12	Jul. 2/87	6765	3222	4820	193	775	126	324	14	43302	43120	0	38	608.7	0.0957
355		Jul. 9/87	6764	3375	4783	174	656	143	435	47	43248	43105	0	34	608.6	0.0957
356		Jul. 16/87	6851	3419	4721	181	707	143	260	28	43280	43114	2	24	608.6	0.0957
357	D3-3	Jun. 30/87	12991	6437	33680	548	2550	216	952	58	21655	21263	1	81	316.4	0.9174
358		Jul. 7/87	12427	6461	32829	539	2494	256	1050	75	21673	21358	1	81	315.9	0.9174
359		Jul. 14/87	12782	6259	33507	553	2464	271	1124	48	21640	21236	0	85	316.1	0.9174
360	D3-4	Jun. 30/87	13574	6764	36319	574	2555	322	1213	167	21655	21176	1	77	317.2	0.9754
361		Jul. 7/87	13424	6817	35735	533	3357	178	1170	132	21673	21269	1	123	317	0.9754
362		Jul. 14/87	13559	6746	35676	565	2599	252	1026	204	21640	21125	0	90	317.1	0.9754
363	D3-5	Jul. 2/87	13008	6545	34175	559	3680	288	1406	38	21651	21315	0	72	316.5	0.9649
364		Jul. 9/87	13290	6588	34284	535	2457	228	1177	89	21624	21250	0	75	316.5	0.9649
365		Jul. 16/87	13390	6538	34887	509	3317	261	1102	40	21640	21189	1	89	316.7	0.9649
366	D3-6	Jul. 2/87	13245	6677	35358	629	3076	194	1658	41	21651	21311	0	56	316.9	0.9714
367		Jul. 9/87	13377	6595	34926	519	2524	230	988	48	21624	21237	0	51	316.6	0.9714
368		Jul. 16/87	13384	6673	35152	539	2405	236	1188	43	21640	21239	1	140	316.8	0.9714
369	D3-9	Jun. 30/87	6281	3035	5738	192	604	95	259	27	43310	43149	2	20	608.5	0.0905
370		Jul. 7/87	6305	3226	5631	159	765	57	560	48	43346	43179	2	46	608.6	0.0905
371		Jul. 14/87	6346	3140	5716	187	1100	72	323	20	43280	43118	0	26	608.5	0.0905
372	D3-10	Jun. 30/87	5933	3016	5672	168	634	126	330	18	43310	43119	2	42	608.6	0.0894
373		Jul. 7/87	6175	3100	5853	129	957	106	347	26	43346	43155	2	24	608.6	0.0894
374		Jul. 14/87	6242	3039	5837	198	671	75	320	15	43280	43042	0	38	608.6	0.0894
375	D3-11	Jul. 2/87	6647	3323	6358	213	728	62	391	10	43302	43095	0	35	609.1	0.0948
376		Jul. 9/87	6611	3436	6207	210	633	76	311	23	43248	43071	0	17	609	0.0948
377		Jul. 16/87	6770	3331	6470	186	634	95	353	19	43280	43058	2	17	609.1	0.0948
378	D3-12	Jul. 2/87	7017	3522	6253	191	589	116	292	18	43302	43092	0	12	609	0.1009

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
379		Jul. 9/87	6895	3519	6316	170	574	90	738	41	43248	43059	0	24	609	0.1009
380		Jul. 16/87	7066	3604	6317	191	664	86	260	18	43280	43139	2	19	609.1	0.1009
381	D4-3	Jun. 30/87	13256	6615	26751	509	2453	200	992	57	21655	21245	1	78	314.6	0.9235
382		Jul. 7/87	13076	6710	27168	541	2184	198	1248	59	21673	21388	1	54	314.7	0.9235
383		Jul. 14/87	13319	6565	26555	571	2418	176	954	63	21640	21265	0	80	314.7	0.9235
384	D4-4	Jun. 30/87	13291	6759	27291	497	2288	157	874	175	21655	21302	1	86	314.6	0.9161
385		Jul. 7/87	13056	6535	25942	562	1915	242	782	42	21673	21413	1	117	313.8	0.9161
386		Jul. 14/87	13434	6539	26753	475	2033	240	1117	77	21640	21239	0	86	314.6	0.9161
387	D4-5	Jul. 2/87	13909	6944	27637	579	1995	219	1133	60	21651	21301	0	77	315.1	0.9701
388		Jul. 9/87	13785	6827	27763	533	2380	308	1034	143	21624	21268	0	52	315.1	0.9701
389		Jul. 16/87	14244	7123	28599	541	2921	219	927	131	21640	21306	1	53	315.5	0.9701
390	D4-6	Jul. 2/87	13527	6685	27039	558	2726	259	931	81	21651	21303	0	84	314.8	0.9516
391		Jul. 9/87	13180	6893	26996	511	2243	240	966	64	21624	21264	0	126	314.7	0.9516
392		Jul. 16/87	13389	6792	26864	481	2610	304	1022	72	21640	21290	1	67	314.8	0.9516
393	D4-9	Jun. 30/87	6437	3315	5040	172	662	94	360	27	43310	43130	2	35	608.6	0.089
394		Jul. 7/87	6574	3118	5095	171	548	128	385	30	43346	43230	2	44	608.6	0.089
395		Jul. 14/87	6510	3259	5103	180	553	79	362	20	43280	43118	0	23	608.6	0.089
396	D4-10	Jun. 30/87	6505	3405	4572	182	584	79	275	92	43310	43186	2	20	608.4	0.091
397		Jul. 7/87	6478	3200	4529	163	471	77	281	59	43346	43187	2	38	608.2	0.091
398		Jul. 14/87	6698	3371	4557	187	504	81	289	14	43280	43177	0	26	608.4	0.091
399	D4-11	Jul. 2/87	6859	3581	4888	187	615	108	469	34	43302	43134	0	14	608.6	0.0954
400		Jul. 9/87	6787	3432	4735	195	671	68	423	9	43248	43124	0	23	608.4	0.0954
401		Jul. 16/87	6576	3515	4792	193	645	88	304	15	43280	43072	2	33	608.4	0.0954
402	D4-12	Jul. 2/87	6216	3143	4353	160	608	81	270	25	43302	43086	0	29	608.4	0.0885
403		Jul. 9/87	6224	3241	4517	195	675	71	238	8	43248	43066	0	12	608.4	0.0885
404		Jul. 16/87	6386	3187	4519	168	548	115	495	5	43280	43134	2	30	608.4	0.0885
405	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
406	Bl-J	Jun. 30/87	67	27	525	0	15	0	12	0	21655	21633	1	0	301.9	
407		Jul. 7/87	5	0	573	0	100	0	26	0	21673	21649	1	0	301.8	
408		Jul. 14/87	100	52	613	0	119	4	23	0	21640	21626	0	0	301.9	
409	Bl-M	Jul. 2/87	8	0	267	0	19	0	4	0	21651	21618	0	0	301.8	
410		Jul. 9/87	36	21	303	0	32	0	40	0	21624	21620	0	0	301.8	
411		Jul. 16/87	50	22	264	0	28	7	12	0	21640	21635	1	0	301.8	
412	Bl-K	Jun. 30/87	35	23	308	0	57	7	23	0	43310	43249	2	7	604.6	
413		Jul. 7/87	93.01	41	388.9	0	86	0	50	0	43346	43296	2	13	604.5	
414		Jul. 14/87	185	76	460	4	90	0	84	0	43280	43231	0	0	604.6	
415	Bl-L	Jul. 2/87	131	83	340	0	45	0	68	0	43302	43224	0	7	604.5	
416		Jul. 9/87	84	56	321	0	193	16	43	0	43248	43206	0	8	604.4	
417		Jul. 16/87	256	113	446	0	59	15	11	0	43280	43212	2	13	604.5	
418																
419	E1-3'	Apr. 2/87	15780	8056	18938	597	1816	247	1127	47	21898	21570	0	100	313.8	0.9294
420		Apr. 9/87	16070	8066	20027	532	1991	319	1069	95	21858	21557	0	26	314.2	0.9294
421		Apr. 16/87	15379	7856	18914	573	1804	278	788	42	21858	21570	0	63	313.5	0.9294
422	E1-4'	Mar. 26/87	15647	7799	19422	582	2315	245	735	43	21898	21592	1	65	313.7	0.934
423		Apr. 7/87	15932	7831	19064	505	2315	280	795	201	21898	21529	0	77	313.7	0.934
424		Apr. 14/87	15471	7744	18977	542	1778	287	785	45	21859	21586	0	44	313.5	0.934
425	E1-7'	Apr. 2/87	15689	7915	19065	637	2420	245	707	42	21898	21588	0	60	313.5	0.9427
426		Apr. 9/87	16241	8034	19595	571	1980	312	965	47	21858	21483	0	91	313.9	0.9427
427		Apr. 16/87	15927	7801	18627	538	1617	362	900	72	21858	21526	0	81	313.5	0.9427
428	E1-8'	Mar. 26/87	15831	8203	20278	583	1988	252	950	169	21898	21569	1	81	314.2	0.934
429		Apr. 7/87	16013	7993	19378	498	2019	527	819	117	21898	21616	0	49	313.8	0.934
430		Apr. 14/87	15638	7529	18927	566	1672	207	1456	60	21859	21557	0	66	313.6	0.934
431	E1-9'	Apr. 2/87	7637	3772	3458	173	822	215	315	77	43796	43608	0	28	608.6	0.0921
432		Apr. 9/87	7671	3738	3436	204	432	98	244	17	43717	43580	0	28	608.5	0.0921

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
433		Apr. 16/87	7696	3903	3348	177	679	150	337	20	43715	43550	0	39	608.7	0.0921
434	E1-10'	Mar. 26/87	7190	3710	3195	171	420	105	309	63	43795	43620	.2	30	608.6	0.0854
435		Apr. 7/87	7447	3678	3126	161	677	196	334	26	43796	43567	0	17	608.7	0.0854
436		Apr. 14/87	7288	3649	3352	155	585	124	299	33	43718	43546	0	30	608.6	0.0854
437	E1-11'	Mar. 26/87	8056	4076	3577	224	514	124	329	6	43795	43656	2	12	608.8	0.0988
438		Apr. 7/87	8057	4012	3659	207	585	104	264	91	43796	44360	0	7	608.7	0.0988
439		Apr. 14/87	8201	4117	3598	189	629	100	328	54	43718	43519	0	34	608.7	0.0988
440	E1-14'	Apr. 2/87	6970	3552	3129	167	368	95	328	32	43796	41122	0	4	608.1	0.0894
441		Apr. 9/87	7210	3629	3269	189	466	115	296	10	43717	43555	0	20	608.3	0.0894
442		Apr. 16/87	6922	3603	3060	149	488	56	337	7	43715	43569	0	29	608.1	0.0894
443	E2-4'	Apr. 2/87	14132	6958	7574	616	994	299	400	41	21898	21682	0	76	310.1	0.9473
444		Apr. 9/87	14528	7126	7658	605	1123	271	881	150	21858	21668	0	45	310.3	0.9473
445		Apr. 16/87	14013	7009	7032	572	960	351	508	50	21858	21598	0	76	309.9	0.9473
446	E2-5'	Apr. 2/87	14092	6999	7467	569	893	176	590	259	21898	21683	0	47	310	0.9439
447		Apr. 9/87	14346	7283	7893	632	964	281	650	35	21858	21612	0	48	310.3	0.9439
448		Apr. 16/87	14138	7031	7302	562	994	200	641	30	21858	21587	0	80	310	0.9439
449	E2-6'	Mar. 26/87	13623	6938	7025	579	1125	212	482	30	21898	21707	1	56	309.8	0.9318
450		Apr. 7/87	14209	7102	7741	595	980	226	665	189	21898	21590	0	81	310.1	0.9318
451		Apr. 14/87	13912	6811	7108	593	1150	189	748	144	21859	21682	0	30	309.8	0.9318
452	E2-8'	Mar. 26/87	13773	6986	7343	582	1742	233	540	75	21898	21701	1	39	309.9	0.9486
453		Apr. 7/87	14325	7205	7525	586	832	217	644	169	21898	21589	0	71	310.2	0.9486
454		Apr. 14/87	13957	7023	6931	630	1339	144	485	79	21859	21648	0	100	309.8	0.9486
455	E2-9'	Apr. 2/87	6688	3310	1648	186	410	100	131	25	43796	43727	0	11	607.6	0.0889
456		Apr. 9/87	6755	3387	1493	169	404	93	284	9	43717	43624	0	27	607.7	0.0889
457		Apr. 16/87	6519	3308	1497	183	432	43	296	12	43715	43603	0	32	607.5	0.0889
458	E2-10'	Apr. 2/87	6212	3092	1368	173	292	55	203	12	43796	43665	0	18	607.6	0.0878
459		Apr. 9/87	6181	3141	1365	194	404	100	315	22	43717	43564	0	16	607.6	0.0878

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
460		Apr. 16/87	6249	3028	1329	171	425	55	214	49	43715	43614	0	19	607.4	0.0878
461	E2-11'	Mar. 26/87	6111	3099	1465	150	89	95	351	91	43795	43651	2	20	607.4	0.0858
462		Apr. 7/87	6308	3248	1477	184	505	99	468	21	43796	43573	0	39	607.4	0.0858
463		Apr. 14/87	6244	3145	1481	156	326	68	216	54	43718	43547	0	26	607.3	0.0858
464	E2-13'	Mar. 26/87	6886	3310	1483	176	340	124	216	16	43795	43595	2	33	607.8	0.0929
465		Apr. 7/87	6992	3439	1566	195	324	76	265	35	43796	43622	0	12	607.7	0.0929
466		Apr. 14/87	6629	3390	1410	177	301	94	397	33	43718	43594	0	32	607.5	0.0929
467	E3-4'	Mar. 26/87	13751	6908	9238	610	996	204	495	25	21898	21656	1	44	310.3	0.9325
468		Apr. 7/87	13776	6972	9271	565	1097	162	677	36	21898	21685	0	112	310.4	0.9325
469		Apr. 14/87	13973	6863	9457	561	1016	270	527	130	21859	21582	0	114	310.4	0.9325
470	E3-5'	Mar. 26/87	13782	6980	9566	533	952	230	578	90	21898	21581	1	60	310.6	0.9261
471		Nov. 17/87	13479	6764	9397	613	355	175	600	33	21824	21648	2	36	310.6	0.9261
472		Apr. 14/87	13735	6933	9463	559	1204	225	544	161	21859	21652	0	83	310.4	0.9261
473	E3-6'	Apr. 2/87	14076	7157	9631	601	1708	260	604	47	21898	21664	0	96	310.7	0.9487
474		Apr. 9/87	13963	6915	9347	587	1054	195	520	54	21858	21699	0	23	310.5	0.9487
475		Apr. 16/87	14055	6990	9689	572	1250	459	508	18	21858	21563	0	76	310.7	0.9487
476	E3-7'	Apr. 2/87	13929	7073	9518	558	984	281	625	68	21898	21683	0	68	310.6	0.9416
477		Apr. 9/87	13810	7012	9772	610	1151	255	760	33	21858	21649	0	11	310.6	0.9416
478		Apr. 16/87	14182	6927	10227	625	1180	236	584	90	21858	21580	0	55	310.8	0.9416
479	E3-9'	Mar. 26/87	6369	3319	2327	193	357	95	175	77	43795	43663	2	23	607.8	0.0897
480		Apr. 7/87	6495	3214	2194	208	428	150	261	23	43796	43215	0	6	607.8	0.0897
481		Apr. 14/87	6404	3258	2075	155	390	117	242	23	43718	43631	0	10	607.7	0.0897
482	E3-10'	Apr. 2/87	6586	3276	1819	200	244	104	228	16	43796	43659	0	16	607.7	0.0859
483		Apr. 9/87	6329	3314	1708	187	410	81	206	23	43717	43598	0	18	607.6	0.0859
484		Apr. 16/87	6300	3173	1716	168	408	78	331	81	43715	43629	0	33	607.5	0.0859
485	E3-11'	Mar. 26/87	6517	3260	1996	205	425	77	404	42	43795	43619	2	32	608	0.0921
486		Apr. 7/87	6620	3306	1927	190	386	81	221	78	43796	43571	0	42	607.9	0.0921

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
487		Apr. 14/87	6919	3411	2029	186	532	46	244	62	43718	43606	0	25	608.1	0.0921
488	E3-14'	Apr. 2/87	6621	3349	2307	208	436	90	329	6	43796	43688	0	25	607.8	0.0917
489		Apr. 9/87	7000	3391	2346	197	376	138	302	72	43717	43542	0	48	607.9	0.0917
490		Apr. 16/87	6785	3440	2295	209	412	75	233	63	43715	43608	0	27	607.8	0.0917
491	E4-3'	Mar. 26/87	14177	7103	10845	618	1061	297	646	65	21898	21700	1	38	311.1	0.9447
492		Apr. 7/87	13850	7070	10851	570	1368	181	603	62	21898	21569	0	116	310.9	0.9447
493		Apr. 14/87	14194	7129	10841	616	2112	259	548	52	21859	21625	0	81	311	0.9447
494	E4-6'	Apr. 2/87	13904	6974	10977	588	1344	293	684	135	21898	21674	0	48	311	0.936
495		Apr. 9/87	13966	6898	10664	639	1204	259	693	46	21858	21601	0	49	310.8	0.936
496		Apr. 16/87	13918	6878	11093	615	1103	278	624	132	21858	21567	0	67	310.9	0.936
497	E4-7'	Mar. 26/87	13998	7025	10797	538	2002	234	633	196	21898	21665	1	81	310.9	0.9487
498		Apr. 7/87	14252	7360	11740	589	1521	257	698	105	21898	21563	0	67	311.3	0.9487
499		Apr. 14/87	14016	7088	10772	597	1305	240	680	55	21859	21576	0	76	310.8	0.9487
500	E4-8'	Apr. 2/87	13942	6815	11262	609	1192	147	548	33	21898	21597	0	64	310.9	0.9398
501		Apr. 9/87	14084	6867	10807	613	2048	300	719	70	21858	21597	0	53	310.9	0.9398
502		Apr. 16/87	13766	7088	10709	603	1196	214	578	67	21858	21598	0	60	310.8	0.9398
503	E4-9'	Apr. 2/87	6331	3110	1836	170	608	125	185	18	43796	43712	0	20	607.5	0.0882
504		Apr. 9/87	6565	3228	1970	197	368	104	204	9	43717	43602	0	15	607.7	0.0882
505		Apr. 16/87	6193	3132	1911	184	530	168	191	33	43715	43580	0	28	607.6	0.0882
506	E4-10'	Mar. 26/87	7087	3422	2151	211	368	72	199	81	43795	43678	2	27	608	0.0995
507		Apr. 7/87	6872	3544	2199	245	371	53	248	6	43796	43624	0	14	608.1	0.0995
508		Apr. 14/87	6775	3395	2137	172	408	152	230	4	43718	43526	0	42	607.9	0.0995
509	E4-11'	Mar. 26/87	7233	3466	2364	208	452	110	221	84	43795	43609	2	86	607.9	0.0975
510		Apr. 7/87	7305	3702	2388	220	416	94	204	39	43796	43578	0	43	608	0.0975
511		Apr. 14/87	7413	3663	2290	239	500	89	284	14	43718	43624	0	10	607.9	0.0975
512	E4-12'	Apr. 2/87	6960	3481	2063	187	558	115	318	16	43796	43671	0	34	607.9	0.091
513		Apr. 9/87	6830	3497	2057	173	485	14	690	24	43717	43614	0	22	607.8	0.091

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
514		Apr. 16/87	7126	3587	2096	203	388	72	281	17	43715	43579	0	23	607.9	0.091
515	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
516	Bl-F	Apr. 2/87	206	94	418	0	135	0	63	0	43796	43688	0	7	604.8	
517		Apr. 9/87	139	73	416	0	170	0	4	0	43717	43686	0	0	604.6	
518		Apr. 16/87	390	208	542	0	109	0	44	0	43715	43634	0	10	604.7	
519	Bl-H	Apr. 14/87	194	70	642	0	142	29	96	0	43718	43667	0	0	604.6	
520		Nov. 17/87	234	121	685	0	26	0	48	0	43649	43621	3	4	604.7	
521	Bl-G	Apr. 2/87	71	51	202	0	25	0	5	0	21898	21869	0	4	301.9	
522		Nov. 17/87	148	53	228	0	8	4	20	0	21824	21820	2	3	301.9	
523		Apr. 16/87	120	75	195	0	35	0	14	0	21858	21854	0	3	301.9	
524	Bl-I	Apr. 7/87	47	17	290	0	46	0	23	0	21898	21852	0	0	301.9	
525		Apr. 14/87	91	49	284	0	46	0	4	0	21859	21836	0	7	301.9	
526		Nov. 17/87	95	49	302	0	30	0	9	0	21824	21797	2	4	301.9	

A1.2 Raw Data For INAA Experiments Performed on Glass Panes

This section contains results for the INAA experiments described in section 2.2.6. AFG- and Pittsburgh-produced glass panes were analysed for sodium, aluminum and calcium. Results for the AFG samples appear in rows 3 to 39 while the Pittsburgh results are shown in rows 41 to 97. Subsample labels are contained in column A. Numbers to the left of the hyphen indicate a glass pane, the numbers to the right are subsample designations. Section A1.1 of this appendix should be consulted for a description of the values appearing in each of the remaining columns. All of the above values were taken directly from output produced by a spectral peak searching routine (PREP 10) supplied by Nuclear Data. Blank values appear at the end of each data set and are separated from the subsamples of a particular flat glass manufacturer by a dashed line. A blank line separates the glasses produced by each manufacturer.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Sub-	Date	Raw	Cou	nts		Bkgrd.	Co	unts		Plsr.	Plsr.	Bkgrd.	Bkgrd.	ClockTime	Mass
2	sample		Na-1	Na-2	Al	Ca	Na-1	Na-2	Al	Ca	Cnts. 1	Cnts. 2	Cnts. 1	Cnts. 2	(seconds)	(mg)
3	4-3	2-May-89	14008	7222	27254	580	2153	275	950	158	21684	21206	0	13	315.7	0.9838
4	4-4	Apr. 27/89	14263	7319	28224	572	2945	235	1034	50	21794	21341	0	127	315.8	0.9838
5	4-5	2-May-89	14391	7220	27860	616	2220	259	976	96	21684	21393	0	25	315.8	0.9813
6	4-6	Apr. 27/89	14427	7211	27571	615	2016	285	937	32	21794	21492	0	68	315.7	0.9839
7	6-3	2-May-89	14235	7065	26855	580	2186	237	978	96	21684	21458	0	50	315.4	0.9818
8	6-4	2-May-89	14389	7101	27477	593	2336	276	1190	18	21684	21508	0	68	315.7	0.9897
9	6-5	Apr. 27/89	14333	7184	27352	555	3055	325	990	81	21794	21447	0	59	315.6	0.9818
10	6-6	Apr. 27/89	14449	7324	27487	590	2079	301	956	38	21794	21413	0	109	315.7	0.9903
11	13-3	2-May-89	14410	7266	27145	607	2224	252	1094	165	21684	21230	0	18	315.7	0.9899
12	13-4	Apr. 27/89	14419	7078	27446	583	2081	331	977	52	21794	21499	0	123	315.4	0.9829
13	13-5	2-May-89	14467	7095	27914	613	2465	219	1015	72	21684	21468	0	63	315.7	0.9894
14	13-6	Apr. 27/89	14288	7128	27139	598	1999	493	941	99	21794	21466	0	59	315.5	0.9925
15	15-3	Apr. 27/89	14276	7121	27502	553	2250	268	878	52	21794	21426	0	68	315.6	0.9839
16	15-4	Apr. 27/89	14257	7347	27159	573	3005	238	956	67	21794	21491	0	63	315.5	0.9911
17	15-5	2-May-89	14127	7086	27567	542	2273	325	1055	188	21684	21490	0	100	315.5	0.9828
18	15-6	2-May-89	14882	7465	28546	631	2605	242	978	48	21684	21341	0	158	316.2	0.9915
19	4-9	2-May-89	6635	3495	4659	215	815	83	310	17	43368	43412	0	20	608.6	0.0937
20	4-10	Apr. 27/89	7270	3644	4984	225	503	128	327	33	43588	43431	0	41	608.9	0.0991
21	4-11	2-May-89	7503	3665	5002	198	624	105	522	73	43368	43475	0	17	609	0.101
22	4-12	Apr. 27/89	7359	3613	5015	193	580	120	304	61	43588	43421	0	43	609.1	0.101
23	6-9	2-May-89	6880	3546	4969	203	491	57	202	19	43368	43459	0	43	608.7	0.0945
24	6-10	2-May-89	6993	3564	5212	204	822	100	300	16	43368	43421	0	33	608.9	0.096
25	6-11	Apr. 27/89	7856	4110	5434	235	786	195	514	30	43588	43459	0	20	609.3	0.1042
26	6-12	Apr. 27/89	7609	3990	5375	214	671	154	486	16	43588	43389	0	149	609.8	0.1055
27	13-9	2-May-89	6723	3324	4561	177	510	149	232	56	43368	43403	0	4	608.4	0.0906

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
28	13-10	Apr. 27/89	6658	3366	4563	198	727	119	483	38	43588	43436	0	28	608.6	0.0942
29	13-11	2-May-89	7548	3810	5278	215	790	105	347	85	43368	43439	0	7	608.9	0.1002
30	13-12	Apr. 27/89	7332	3551	4964	198	713	95	264	34	43588	43408	0	20	608.7	0.0964
31	15-9	Apr. 27/89	7206	3690	4767	199	581	81	272	69	43588	43411	0	36	608.9	0.0981
32	15-10	Apr. 27/89	7020	3553	4752	195	612	155	330	25	43588	43443	0	34	608.6	0.0957
33	15-11	2-May-89	7820	4076	5366	242	680	169	314	29	43368	43407	0	34	609.3	0.1088
34	15-12	2-May-89	6962	3488	4982	198	918	95	463	35	43368	43417	0	40	608.6	0.0933
35	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
36	Bla-2	Apr. 27/89	75	40	260	0	48	0	23	0	21794	21793	0	0	301.8	
37	Bla-3	2-May-89	24	11	181	0	18	0	0	0	21684	21775	0	0	301.8	
38	Bla-1	Apr. 27/89	118	35	248	0	94	0	44	0	43588	43513	0	15	604.5	
39	Bla-4	2-May-89	89	50	293	0	61	4	34	0	43368	43540	0	5	604.4	
40																
41	1-3	Oct. 11/88	13910	6954	11276	586	1054	187	908	45	21630	21361	2	52	311.2	0.9442
42	1-4	Oct. 25/88	14784	7349	11860	581	1241	295	591	64	21689	21733	2	4	311.6	0.9857
43	1-5	Oct. 25/88	13899	7003	11402	569	1680	167	536	48	21689	21453	2	66	311.1	0.9647
44	1-6	Nov. 1/88	14595	7210	12703	561	1305	342	792	63	21704	21405	2	30	311.9	0.9696
45	8-3	Nov. 8/88	14240	7175	12311	603	1211	326	902	184	21732	21497	0	72	311.7	0.9777
46	8-4	Nov. 8/88	14512	7325	11849	611	3276	265	648	70	21732	21493	0	56	311.7	0.9682
47	8-5	Nov. 8/88	14155	7119	11866	636	1229	238	648	48	21732	21473	0	52	311.5	0.9785
48	8-6	Nov. 8/88	14639	7332	12101	598	1539	198	713	158	21732	21450	0	34	311.7	0.9848
49	13-3	Oct. 11/88	14520	7341	12502	650	1472	228	753	11	21630	21272	2	6	311.8	0.9695
50	13-4	Oct. 25/88	13506	6808	11136	569	1810	209	648	36	21689	21451	2	77	310.9	0.9623
51	13-5	Oct. 25/88	14178	7138	11997	594	1201	204	702	75	21689	21429	2	66	311.4	0.9672
52	13-6	Nov. 15/8	15251	7855	13132	615	1552	230	713	74	21746	21484	0	40	312.4	0.9846
53	37-3	Oct. 11/88	14418	7221	12230	609	1336	229	761	76	21630	21399	2	60	311.6	0.9695
54	37-4	Oct. 25/88	14431	7329	12124	588	1516	207	544	210	21689	21371	2	81	311.6	0.9829

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
55	37-5	Oct. 25/88	14550	7281	11655	634	1705	208	822	45	21689	21485	2	54	311.5	0.9802
56	37-6	Nov. 1/88	14958	7466	12120	639	1216	293	684	40	21704	21420	2	45	311.7	0.9771
57	41-3	Oct. 11/88	14376	7309	12419	654	1148	196	863	66	21630	21453	2	34	311.3	0.9542
58	41-4	Oct. 25/88	14235	7025	11878	625	1748	242	1109	74	21689	21405	2	77	311.4	0.9837
59	41-5	Oct. 25/88	13676	6944	11617	673	1472	278	788	32	21689	21415	2	63	311.1	0.9525
60	41-6	Nov. 1/88	14381	7110	12176	573	1168	234	653	56	21704	21450	2	68	311.5	0.9647
61	48-3	Nov. 8/88	14436	7320	11934	638	1696	405	635	28	21732	21523	0	56	311.5	0.9831
62	48-4	Nov. 8/88	14944	7382	11965	677	1352	316	600	17	21732	21441	0	98	311.8	0.9834
63	48-5	Nov. 8/88	14495	7411	11851	633	1316	398	616	60	21732	21528	0	63	311.4	0.972
64	48-6	Nov. 8/88	14214	7375	11873	635	1539	276	1117	130	21732	21487	0	99	311.6	0.9696
65	1-9	Oct. 11/88	7198	3605	3276	227	518	110	266	26	43260	43077	4	24	608.8	0.0998
66	1-10	Oct. 25/88	7697	3947	2573	186	421	96	332	179	43378	43251	4	24	608.3	0.1065
67	1-11	Oct. 25/88	8178	4072	2642	215	551	115	273	15	43378	43210	4	20	609	0.1137
68	1-12	Nov. 1/88	6906	3471	2197	164	416	124	385	38	43407	43242	3	33	607.8	0.0909
69	8-9	Nov. 8/88	7579	3838	2500	210	493	150	236	34	43464	43357	0	115	608.2	0.1021
70	8-10'	Nov. 15/8	7042	3587	2250	188	394	86	266	26	43491	43359	0	28	608	0.0904
71	8-11	Nov. 8/88	6889	3493	2108	207	383	86	295	55	43464	43337	0	16	607.9	0.0902
72	8-12	Nov. 15/8	7942	4013	2896	255	630	162	217	19	43491	43330	0	35	608.7	0.105
73	13-9	Oct. 11/88	7203	3558	2722	213	439	138	280	11	43260	43067	4	30	608.6	0.0965
74	13-10	Oct. 25/88	7914	3838	2724	216	523	109	224	11	43378	43220	4	20	608.6	0.1029
75	13-11	Oct. 25/88	7363	3818	3079	216	628	81	319	16	43378	43238	4	49	608.7	0.1017
76	13-12	Nov. 1/88	7327	3587	2309	217	499	86	191	6	43407	43297	3	66	608.2	0.0985
77	37-9	Oct. 11/88	7922	4066	3657	242	708	176	323	16	43260	43120	4	24	609	0.1097
78	37-10	Nov. 1/88	7923	3951	2642	212	459	128	374	46	43407	43262	3	28	608.2	0.1025
79	37-11	Oct. 25/88	7925	4040	2511	223	448	114	357	30	43378	43172	4	18	608.7	0.1073
80	37-12	Nov. 1/88	7604	3810	2204	235	484	173	252	0	43407	43239	3	46	608.4	0.1057
81	41-9	Oct. 11/88	7082	3462	2238	171	378	126	312	32	43260	43113	4	17	608.3	0.0936

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
82	41-10	Oct. 25/88	7826	4018	2517	244	480	122	259	26	43378	43235	4	26	608.2	0.1067
83	41-11	Oct. 25/88	7242	3586	2590	214	537	75	257	28	43378	43244	4	29	608.3	0.0984
84	41-12	Nov. 1/88	7113	3585	2658	220	432	77	244	26	43407	43263	3	20	608	0.0955
85	48-9	Nov. 8/88	7264	3710	2400	212	440	150	238	26	43464	43289	0	23	608.3	0.0954
86	48-10	Nov. 8/88	7207	3566	2252	204	412	89	400	26	43464	43291	0	16	608.3	0.0967
87	48-11'	Nov. 15/8	8058	4035	2945	188	604	72	315	45	43491	43347	0	64	608.6	0.1084
88	48-12	Nov. 8/88	8031	4040	2807	232	416	100	298	43	43464	43319	0	23	608.6	0.1049
89	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
90	Bl-3	Nov. 15/8	68	20	249	0	15	0	22	0	21746	21732	0	4	301.8	
91	Bl-3	Nov. 1/88	53	22	280	0	47	0	20	0	21704	21696	2	0	301.8	
92	Bl-4	Nov. 8/88	43	19	374	0	29	0	0	0	21732	21720	0	0	301.9	
93	Bl-4	Oct.25/88	12	0	234	0	18	0	5	0	21689	21685	2	0	301.8	
94	Bl-9	Nov. 15/8	61	50	463	0	75	0	41	0	43491	43430	0	7	604.3	
95	Bl-9	Nov. 1/88	136	58	465	0	67	16	63	0	43407	43364	3	6	604.3	
96	Bl-10	Nov. 8/88	150	60	637	0	152	12	49	0	43464	43415	0	10	604.5	
97	Bl-10	Oct. 25/88	164	94	523	0	81	0	54	0	43378	43295	4	3	604.6	

Appendix 2

Three sections are contained in this appendix. The first section deals with the cyclic instrumental neutron activation analysis (CINAA) experiments performed on 15 glass samples supplied by an RCMP forensic laboratory. Contained in the second section are raw data for the analysis by CINAA of panes produced by two major Canadian flat glass manufacturers. Both sections report the results for hafnium analyses as described in chapter 3. The last section is a table of thermal neutron reactions that may be studied by CINAA.

A2.1 Raw Data For CINAA Experiments Performed on Fifteen Glass Samples

This section contains results for the CINAA experiments described in sections 3.2.1 to 3.2.4. Fifteen glass samples provided by an RCMP forensic laboratory were analysed for hafnium. Column A contains subsample labels. Glass samples are indicated by letters and numbers appearing to the left of the hyphen while numbers on the right designate a subsample. Analysis dates for each subsample are contained in column B. Appearing in column C are the raw counts for hafnium while column D lists background counts underlying this photopeak. Average pulser counts (pulser 1) in the absence of a glass subsample are indicated in column E. This value was obtained by averaging the pulser counts obtained prior to and immediately following a day's experiments. Pulser 2 (column F) was the designation employed when the same pulser was counted during the acquisition of a glass subsample spectrum. Background counts associated with the two pulser peaks appear in columns G and H. Live times are listed in column I and the clock times were

either 300 (1-mg subsamples) or 120 seconds (5-mg subsamples) in duration. All of the above values were taken directly from output produced by a spectral peak searching routine (PREP 10) supplied by Nuclear Data. Finally, appearing in column J are the subsample masses in milligrams. The uncertainty associated with every measurement is ± 0.0017 milligrams. Blank values listed at the end of each data set are separated from the subsamples for a particular refractive index group by a dashed line. A blank line separates glasses with different refractive index values.

	A	B	C	D	E	F	G	H	I	J
1	Sub-	Date	Raw Counts	Bkgrd. Counts	Plsr.	Plsr.	Bkgrd.	Bkgrd.	Live Time	Mass
2	sample		Hf	Hf	Cnts. 1	Cnts. 2	Cnts. 1	Cnts. 2	(seconds)	(mg)
3	A1-50	Apr. 14/88	1848	5240	17999	16919	8	2061	283.15	1.0075
4		Apr. 26/88	2095	5595	17938	16905	22	2018	283.63	1.0075
5		5-May-88	2350	5933	17995	16745	24	2103	282.03	1.0075
6	A1-51	12-May-88	2185	5595	17980	16899	30	2040	282.99	1.003
7		Apr. 26/88	2488	5580	17988	16959	22	2030	283.66	1.003
8		5-May-88	2129	5613	17995	16939	24	1854	283.37	1.003
9	A1-52	Apr. 28/88	2794	6390	17986	16648	20	2289	281.26	1.0065
10		12-May-88	2294	5423	17980	16801	30	1999	283.39	1.0065
11		19-May-88	2328	5700	18003	16799	14	1923	283.65	1.0065
12	A1-53	Apr. 28/88	2424	5238	17986	16836	20	1994	282.75	1.007
13		12-May-88	2307	5623	17980	16647	30	2328	282.92	1.007
14		19-May-88	2138	2011	18003	16813	14	2352	284.51	1.007
15	A1-55	Apr. 14/88	2460	3128	7200	6397	3	1697	109.23	4.972
16		Apr. 26/88	2779	3692	7195	6484	9	1603	109.29	4.972
17		5-May-88	2601	3048	7198	6346	10	2213	109.36	4.972
18	A1-56	Apr. 14/88	2542	3043	7200	6488	3	1833	109.32	4.9525
19		Apr. 26/88	2576	2925	7195	6417	9	1686	109.58	4.9525
20		5-May-88	2481	3183	7198	6502	10	1719	109.27	4.9525
21	A1-57	Apr. 28/88	2293	3165	7194	6359	8	2077	109.42	4.9595
22		12-May-88	2538	2850	7192	6526	12	1820	109.63	4.9595
23		19-May-88	2561	1202	7201	6309	5	1902	109.47	4.9595
24	A1-58	Apr. 28/88	3483	1166	7194	6319	8	1872	109.57	4.976
25		12-May-88	3568	3290	7192	6388	12	1782	108.97	4.976
26		19-May-88	3718	3233	7201	6308	5	1917	109.07	4.976
27	A2-50	Apr. 14/88	1738	5623	17999	16642	8	2301	281.39	1.027

	A	B	C	D	E	F	G	H	I	J
28		Apr. 26/88	1802	5218	17988	16730	22	2286	282.17	1.027
29		5-May-88	2104	6180	17995	16545	24	2574	280.88	1.027
30	A2-51	Apr. 14/88	1692	6498	17999	16659	8	2148	281.48	1.0165
31		Apr. 26/88	2432	5743	17988	16742	22	2021	282.15	1.0165
32		5-May-88	1789	6018	17995	16719	24	2702	281.3	1.0165
33	A2-52	Apr. 28/88	1875	2363	17986	16690	20	2197	282.62	1.007
34		12-May-88	1776	5141	17980	16797	30	2130	281.81	1.007
35		19-May-88	1810	5130	18003	16672	14	2274	282.22	1.007
36	A2-53	Apr. 28/88	2095	5733	17986	16759	20	2353	281.96	1.024
37		12-May-88	1780	6033	17980	16624	30	2616	281.08	1.024
38		19-May-88	1648	5337	18003	16827	14	2434	282.32	1.024
39	A2-55	Apr. 14/88	1819	3283	7200	6345	3	2088	108.39	4.961
40		Apr. 26/88	1857	3255	7195	6501	9	2080	108.23	4.961
41		5-May-88	1697	3365	7198	6355	10	1843	108.07	4.961
42	A2-56	Apr. 14/88	1510	2970	7200	6549	3	2016	109.48	4.9705
43		Apr. 26/88	1971	3268	7195	6265	9	1953	108.07	4.9705
44		5-May-88	2102	3290	7198	6395	10	2001	107.89	4.9705
45	A2-57	Apr. 28/88	2031	3228	7194	6331	8	2366	108.06	4.9695
46		12-May-88	1904	3140	7192	6380	12	1980	107.94	4.9695
47		19-May-88	1712	3068	7201	6350	5	1947	108.86	4.9695
48	A2-58	Apr. 28/88	1705	1258	7194	6372	8	3413	108.34	4.961
49		12-May-88	1878	1251	7192	6361	12	2031	108.24	4.961
50		19-May-88	1734	3363	7201	6472	5	1807	108.12	4.961
51	A3-50	Apr. 14/88	1999	5641	17999	16856	8	2415	281.4	1.022
52		Apr. 26/88	1970	5718	17988	16755	22	2007	282.84	1.022
53		5-May-88	2207	5629	17995	16691	24	2513	281.32	1.022
54	A3-51	Apr. 14/88	2243	6060	17999	16781	8	1909	282.59	1.0105

	A	B	C	D	E	F	G	H	I	J
55		Apr. 26/88	2153	5479	17988	16823	22	2184	281.87	1.0105
56		5-May-88	2553	5688	17995	16661	24	2483	282.21	1.0105
57	A3-52	Apr. 28/88	2159	2201	17986	16925	20	1857	283.3	1.0115
58		12-May-88	1957	5420	17980	16784	30	2109	281.89	1.0115
59		19-May-88	2438	2314	18003	16526	14	2235	282.39	1.0115
60	A3-53	Apr. 28/88	2458	5948	17986	16768	20	1834	281.9	1.0145
61		12-May-88	2304	5798	17980	16673	30	2431	282.14	1.0145
62		19-May-88	2575	6777	18003	16848	14	2359	283.13	1.0145
63	A3-55	Apr. 14/88	2570	3383	7200	6372	3	1986	108.82	4.9545
64		Apr. 26/88	2358	3155	7195	6449	9	1658	108.85	4.9545
65		5-May-88	2319	5220	7198	6346	10	2145	108.86	4.9545
66	A3-56	Apr. 14/88	2152	3259	7200	6647	3	2093	109.17	4.968
67		Apr. 26/88	2305	3018	7195	6395	9	1675	109.26	4.968
68		5-May-88	2351	3523	7198	6378	10	1821	108.82	4.968
69	A3-57	Apr. 28/88	2453	3065	7194	6467	8	1866	108.83	4.9555
70		12-May-88	2316	3035	7192	6528	12	1812	108.88	4.9555
71		19-May-88	2427	3322	7201	6312	5	2181	109.17	4.9555
72	A3-58	Apr. 28/88	2325	3297	7194	6505	8	1911	109.09	4.944
73		12-May-88	2229	3170	7192	6414	12	1947	109.05	4.944
74		19-May-88	2490	3308	7201	6350	5	2139	109.06	4.944
75	A5-50	Apr. 14/88	1656	5553	17999	16913	8	1947	283.03	0.9965
76		Apr. 26/88	1636	4802	17988	16962	22	1755	284.58	0.9965
77		5-May-88	1581	5108	17995	16831	24	1713	283.76	0.9965
78	A5-51	Apr. 14/88	1383	4817	17999	16852	8	2025	284.28	1.019
79		Apr. 26/88	1773	5087	17988	16890	22	1770	283.57	1.019
80		5-May-88	1887	5353	17995	16855	24	1776	284.37	1.019
81	A5-52	31-May-88	1817	5348	17976	16935	24	1611	284.56	1.005

	A	B	C	D	E	F	G	H	I	J
82		12-May-88	2024	5285	17980	16881	30	1590	284.4	1.005
83		19-May-88	2101	5748	18003	16699	14	2113	283.14	1.005
84	A5-53	Apr. 28/88	1878	2210	17986	16953	20	1898	283.6	1.011
85		12-May-88	1285	5123	17980	16875	30	2072	283.56	1.011
86		19-May-88	1278	4700	18003	16872	14	1863	284.66	1.011
87	A5-55	Apr. 14/88	1318	2940	7200	6565	3	1542	110.1	4.978
88		Apr. 26/88	1560	2890	7195	6395	9	1674	109.74	4.978
89		5-May-88	1480	2840	7198	6449	10	1546	109.88	4.978
90	A5-56	Apr. 14/88	1502	2885	7200	6443	3	1671	109.81	4.9605
91		Apr. 26/88	1274	2635	7195	6492	9	1581	110.05	4.9605
92		5-May-88	1204	2823	7198	6487	10	1416	110.55	4.9605
93	A5-57	Apr. 28/88	1223	3118	7194	6589	8	1684	109.85	4.9755
94		12-May-88	1223	2995	7192	6454	12	1497	110.73	4.9755
95		19-May-88	1473	2795	7201	6351	5	1614	110.02	4.9755
96	A5-58	Apr. 28/88	1443	3006	7194	6520	8	1593	110.08	4.9585
97		12-May-88	1382	3043	7192	6396	12	1862	109.6	4.9585
98		19-May-88	1334	2750	7201	6465	5	2209	110.27	4.9585
99	---	---	---	---	---	---	---	---	---	---
100	Bl-32	Apr. 14/88	631	2812	17999	17454	8	442	291.76	
101		12-May-88	837	3272	17980	17441	30	492	291.58	
102		19-May-88	961	3653	18003	17286	14	573	290.74	
103	Bl-33	Apr. 28/88	660	3460	17986	17291	20	789	289.4	
104		12-May-88	621	3016	17980	17497	30	540	291.03	
105		19-May-88	598	3064	18003	17324	14	690	290.73	
106	Bl-37	Apr. 14/88	339	930	7200	7047	3	105	117.83	
107		Apr. 26/88	356	242	7195	7053	9	196	117.99	
108		5-May-88	504	982	7198	7086	10	105	118.07	

	A	B	C	D	E	F	G	H	I	J
109	Bl-38	Apr. 28/88	413	734	7194	7078	8	127	117.94	
110		31-May-88	417	743	7190	7097	10	81	118.15	
111		19-May-88	402	666	7201	7048	5	176	118.04	
112										
113	C1-50	Jan. 21/88	3864	6122	17842	16692	128	2583	281.85	1.0015
114		Jan. 28/88	3758	6350	17954	16655	20	2664	282.53	1.0015
115		Feb. 9/88	3495	5420	17952	16801	12	2169	283.87	1.0015
116	C1-51	Jan. 21/88	3849	5844	17842	16753	128	2706	282.43	1.0195
117		Jan. 28/88	3790	6594	17954	16705	20	2772	282.1	1.0195
118		Feb. 9/88	3550	5118	17952	16820	12	2088	284.29	1.0195
119	C1-52	Jan. 21/88	3534	5607	17842	16737	128	2646	282.96	1.0005
120		Jan. 26/88	3628	6573	17799	16780	166	3034	281.41	1.0005
121		Feb. 2/88	3434	6218	17928	16771	38	2974	282.36	1.0005
122	C1-53	Jan. 19/88	3503	6642	17928	16691	50	2434	282.31	0.9885
123		Jan. 26/88	3532	6666	17799	16694	166	2486	282.63	0.9885
124		Feb. 2/88	3274	3102	17928	16685	38	3624	280.65	0.9885
125	C1-55	Jan. 21/88	4048	4299	7137	6410	51	1970	107.41	4.9
126		Jan. 28/88	4418	4508	7182	6332	8	2429	107.78	4.9
127		Feb. 16/88	4221	3558	7200	6204	2	2288	107.85	4.9
128	C1-56	Jan. 21/88	4175	4757	7137	6314	51	2543	107.75	4.946
129		Jan. 28/88	4284	4785	7182	6500	8	2325	108.39	4.946
130		Feb. 9/88	4250	3195	7181	6442	5	1664	109.24	4.946
131	C1-57	Jan. 19/88	4128	3966	7171	6272	20	2805	107.5	4.929
132		Jan. 26/88	4444	5967	7120	6276	66	2355	107.17	4.929
133		Feb. 2/88	4305	4748	7171	6319	15	2509	107.64	4.929
134	C1-58	Jan. 19/88	4309	4041	7171	6281	20	2380	107.31	4.9655
135		Jan. 26/88	4234	4332	7120	6404	66	2335	107.03	4.9655

	A	B	C	D	E	F	G	H	I	J
136		Feb. 2/88	4212	5093	7171	6487	15	2468	107.73	4.9655
137	C2-50	Jan. 21/88	3556	7156	17842	16391	128	2909	279.43	1.023
138		Jan. 28/88	3486	6663	17954	16618	20	2814	281.82	1.023
139		Feb. 9/88	3620	6518	17952	16661	12	2265	282.55	1.023
140	C2-51	Jan. 21/88	3691	6457	17842	16545	128	2887	281.17	1.0085
141		Jan. 28/88	3319	6218	17954	16751	20	2730	282.85	1.0085
142		Feb. 9/88	3658	5083	17952	16834	12	2187	284.45	1.0085
143	C2-52	Jan. 19/88	3353	6168	17928	16885	50	2308	281.92	1.029
144		Jan. 26/88	3387	6006	17799	16997	166	2422	283.13	1.029
145		Feb. 11/88	3786	5405	17995	16700	18	2327	282.84	1.029
146	C2-53	Jan. 19/88	3486	6126	17928	16641	50	2748	282.71	1.0105
147		Jan. 26/88	3435	6460	17799	16667	166	2615	281.71	1.0105
148		Feb. 2/88	3245	2806	17928	16744	38	2861	282.77	1.0105
149	C2-55	Jan. 21/88	4051	4729	7137	6244	51	2460	107.41	4.914
150		Jan. 28/88	4276	5512	7182	6249	8	2478	108.05	4.914
151		Feb. 9/88	4172	3240	7181	6399	5	1872	108.44	4.914
152	C2-56	Jan. 21/88	4197	5061	7137	6154	51	2304	106.74	4.9345
153		Feb. 16/88	4106	3513	7200	6279	2	2165	107.83	4.9345
154		Feb. 23/88	4614	3385	7189	6321	9	2285	107.55	4.9345
155	C2-57	Feb. 11/88	4016	1280	7198	6235	7	1708	107.94	4.9515
156		Jan. 26/88	4341	4017	7120	6374	66	2198	107.42	4.9515
157		Feb. 2/88	4022	1614	7171	6238	15	2226	107.68	4.9515
158	C2-58	Jan. 19/88	4141	4005	7171	6405	20	2128	107.93	4.954
159		Jan. 26/88	4278	4436	7120	6212	66	2461	107.45	4.954
160		Feb. 2/88	4547	5089	7171	6207	15	2197	107.5	4.954
161	C3-50	Jan. 21/88	2284	10667	17842	16122	128	3094	275.68	1.0325
162		Jan. 28/88	1817	5490	17954	16828	20	2461	283.19	1.0325

	A	B	C	D	E	F	G	H	I	J
163		Feb. 18/88	1821	5778	17996	16830	14	2308	282.3	1.0325
164	C3-51	Jan. 21/88	2038	6100	17842	16816	128	2342	283	1.033
165		Jan. 28/88	1554	6328	17954	16758	20	2310	282.9	1.033
166		Feb. 9/88	1913	5335	17952	16806	12	1991	283.37	1.033
167	C3-52	Jan. 19/88	1319	4648	17928	17074	50	1757	286.5	1.045
168		Jan. 26/88	1166	4123	17799	17250	166	1781	287.33	1.045
169		Feb. 2/88	1823	4615	17928	17175	38	2095	288.13	1.045
170	C3-53	Jan. 21/88	1433	5063	17842	16723	128	2664	283.71	1.0485
171		Jan. 26/88	1782	7098	17799	16669	166	2499	281.77	1.0485
172		Feb. 2/88	1708	6427	17928	16772	38	2503	282.66	1.0485
173	C3-55	Jan. 21/88	1435	3223	7137	6484	51	1957	108.67	4.9185
174		Jan. 28/88	1222	3882	7182	6396	8	2452	108.83	4.9185
175		Feb. 9/88	1422	3145	7181	6459	5	1731	109.22	4.9185
176	C3-56	Jan. 21/88	1247	1564	7137	6258	51	1893	108.55	4.9745
177		Jan. 28/88	1348	3748	7182	6402	8	2219	107.8	4.9745
178		Feb. 18/88	1269	3352	7198	6475	6	1947	108.78	4.9745
179	C3-57	Jan. 19/88	1273	2718	7171	6422	20	1915	109.57	4.9525
180		Jan. 26/88	1259	2863	7120	6420	66	1693	109.94	4.9525
181		Feb. 2/88	1067	2960	7171	6549	15	1648	110.24	4.9525
182	C3-58	Jan. 19/88	1467	3432	7171	6381	20	2408	108.29	4.974
183		Jan. 26/88	1481	3235	7120	6402	66	2859	108.18	4.974
184		Feb. 2/88	1134	1277	7171	6308	15	2109	109.01	4.974
185	---	---	---	---	---	---	---	---	---	---
186	Bl-50	Jan. 21/88	1583	3102	17842	17528	128	698	292.92	
187		Jan. 28/88	1214	3564	17954	17525	20	676	292.48	
188		Feb. 9/88	1266	1156	17952	17544	12	721	293.04	
189	Bl-51	Jan. 19/88	803	3913	17928	17347	50	949	290.47	

	A	B	C	D	E	F	G	H	I	J
190		Jan. 26/88	775	2958	17799	17500	166	553	292.86	
191		Feb. 2/88	935	1712	17928	17365	38	1430	291.42	
192	Bl-55	Jan. 21/88	460	894	7137	7133	51	168	118.22	
193		Jan. 28/88	299	760	7182	7070	8	195	118.23	
194		Feb. 23/88	684	749	7189	7024	9	20	117.91	
195	Bl-56	Jan. 19/88	312	924	7171	7122	20	150	117.93	
196		Jan. 26/88	221	954	7120	7072	66	247	117.91	
197		Feb. 2/88	467	1051	7171	6938	15	648	117.51	
198										
199	D1-50	Mar. 8/88	1408	5528	17992	16775	26	2184	281.71	1.0065
200		Mar. 15/88	1182	5177	18004	16804	12	2142	282.62	1.0065
201		Mar. 29/88	1426	5396	17984	16744	18	2097	282.19	1.0065
202	D1-51	Mar. 8/88	1842	5613	17992	16857	26	1998	282.59	1.0065
203		Mar. 15/88	1934	5560	18004	16776	12	2184	282.59	1.0065
204		Mar. 22/88	1400	5820	17939	16795	50	1974	282.85	1.0065
205	D1-52	Mar. 17/88	1794	5108	17988	16858	27	2331	282.66	1.0135
206		Mar. 24/88	1304	5893	17994	16705	16	2503	281.42	1.0135
207		Mar. 31/88	1771	5355	17969	16761	32	2082	282.07	1.0135
208	D1-53	Mar. 17/88	1617	5281	17988	16730	27	2001	282.05	1.0185
209		Mar. 24/88	1200	5958	17994	16737	16	2207	282.62	1.0185
210		Mar. 31/88	1468	5558	17969	16915	32	2194	283.2	1.0185
211	D1-55	Mar. 8/88	1479	3068	7197	6394	11	1675	108.91	4.955
212		Mar. 15/88	1424	2860	7202	6441	5	1856	108.79	4.955
213		Mar. 22/88	1414	3140	7176	6361	20	1601	109.06	4.955
214	D1-56	Mar. 8/88	1888	3123	7197	6400	11	1934	108.94	4.9785
215		Mar. 15/88	1531	3205	7202	6360	5	1746	108.87	4.9785
216		Mar. 22/88	1448	3080	7176	6321	20	1973	108.86	4.9785

	A	B	C	D	E	F	G	H	I	J
217	D1-57	Mar. 17/88	1891	3030	7195	6411	11	1911	109.1	4.963
218		Mar. 24/88	1652	3033	7197	6457	6	1674	109.33	4.963
219		Mar. 31/88	1096	2215	7188	6624	13	1484	112.36	4.963
220	D1-58	Mar. 17/88	1454	3394	7195	6373	11	1573	109.04	4.947
221		Mar. 24/88	1343	2860	7197	6412	6	1734	109.39	4.947
222		Mar. 31/88	1463	3612	7188	6384	13	1860	108.75	4.947
223	D2-50	Mar. 8/88	2003	5848	17992	16825	26	2419	282.07	1.0105
224		Mar. 15/88	2404	5790	18004	16864	12	2043	282.32	1.0105
225		Mar. 22/88	1594	5369	17939	16637	50	2223	282.25	1.0105
226	D2-51	Mar. 8/88	1647	5393	17992	16816	26	2163	282.22	0.999
227		Mar. 15/88	1488	5436	18004	16717	12	2103	282.42	0.999
228		Mar. 22/88	1668	5808	17939	16804	50	2886	282.37	0.999
229	D2-52	Mar. 17/88	1970	6135	17988	16835	27	2061	283.4	1.011
230		Mar. 24/88	1644	5036	17994	16819	16	2666	283.23	1.011
231		Mar. 31/88	1858	5189	17969	16973	32	2100	282.99	1.011
232	D2-53	Mar. 17/88	2386	5500	17988	16853	27	2049	283	1.009
233		Mar. 24/88	1919	5040	17994	16972	16	2135	283.69	1.009
234		Apr. 14/88	3190	6259	17999	16797	8	2040	283.35	1.009
235	D2-55	Mar. 8/88	2211	3240	7197	6386	11	2284	108.54	4.974
236		Mar. 15/88	1939	3220	7202	6397	5	1911	108.68	4.974
237		Mar. 22/88	2008	3005	7176	6375	20	2103	108.95	4.974
238	D2-56	Mar. 8/88	1883	3063	7197	6384	11	1612	108.95	4.952
239		Mar. 15/88	1997	2765	7202	6489	5	1707	108.91	4.952
240		Mar. 22/88	2195	3045	7176	6358	20	1908	108.79	4.952
241	D2-57	Mar. 17/88	2112	3133	7195	6399	11	2015	108.78	4.9635
242		Mar. 24/88	2106	3023	7197	6411	6	1815	108.96	4.9635
243		Mar. 31/88	2114	3579	7188	6345	13	1636	109.28	4.9635

	A	B	C	D	E	F	G	H	I	J
244	D2-58	Mar. 17/88	2066	2905	7195	6442	11	1836	108.81	4.9775
245		Mar. 24/88	1964	3484	7197	6563	6	1830	108.96	4.9775
246		Mar. 31/88	2018	3270	7188	6518	13	1856	108.94	4.9775
247	D3-50	Mar. 8/88	1968	2458	17992	16476	26	2637	280.2	0.9995
248		Mar. 15/88	2019	5542	18004	16545	12	2394	280.24	0.9995
249		Mar. 22/88	1687	6193	17939	16644	50	2592	280.66	0.9995
250	D3-51	Mar. 8/88	2162	5630	17992	16590	26	3902	280.91	1.0125
251		Mar. 15/88	1974	6395	18004	16625	12	2613	280.32	1.0125
252		Mar. 22/88	1613	5108	17939	16580	50	2412	281.94	1.0125
253	D3-52	Mar. 17/88	2063	6454	17988	16754	27	2454	281.17	1.014
254		Mar. 24/88	1559	5409	17994	16632	16	2915	281.27	1.014
255		Mar. 31/88	2825	6515	17969	16715	32	2340	280.6	1.014
256	D3-53	Mar. 17/88	2029	5760	17988	16647	27	2905	280.55	1.011
257		Mar. 24/88	2085	2391	17994	16694	16	2409	280.81	1.011
258		Mar. 31/88	1955	5058	17969	16816	32	2206	282.09	1.011
259	D3-55	Mar. 8/88	2229	3308	7197	6177	11	2238	107.31	4.978
260		Mar. 15/88	2208	3535	7202	6235	5	2399	106.8	4.978
261		Mar. 22/88	2030	3443	7176	6241	20	1997	107.32	4.978
262	D3-56	Mar. 8/88	2055	3490	7197	6330	11	2101	107.07	4.9675
263		Mar. 15/88	2242	3408	7202	6309	5	2199	106.96	4.9675
264		Mar. 22/88	2043	3693	7176	6195	20	2442	107.03	4.9675
265	D3-57	Mar. 17/88	2011	3535	7195	6327	11	2412	107.13	4.962
266		Mar. 24/88	2033	4098	7197	6154	6	2438	106.69	4.962
267		Mar. 31/88	2097	3480	7188	6286	13	2650	107.2	4.962
268	D3-58	Mar. 17/88	2630	3979	7195	6237	11	2298	107.12	4.9525
269		Mar. 24/88	2123	3470	7197	6348	6	2223	106.97	4.9525
270		Mar. 31/88	1700	3691	7188	6356	13	2191	108.03	4.9525

	A	B	C	D	E	F	G	H	I	J
271	D4-50	Mar. 8/88	1954	5342	17992	16825	26	1920	282.45	1.004
272		Mar. 15/88	1696	5612	18004	16771	12	2132	282.14	1.004
273		Mar. 22/88	1919	5348	17939	16788	50	2880	282.55	1.004
274	D4-51	Mar. 8/88	2179	5555	17992	16660	26	2208	281.31	0.9975
275		Mar. 15/88	2052	5103	18004	16801	12	1998	282.89	0.9975
276		Mar. 22/88	2029	5725	17939	16735	50	2151	282.28	0.9975
277	D4-52	Mar. 17/88	2063	5840	17988	16698	27	2334	281.81	1.0225
278		Mar. 24/88	1890	5274	17994	16753	16	2168	282.03	1.0225
279		Mar. 31/88	1929	5159	17969	16744	32	1944	282.98	1.0225
280	D4-53	Mar. 17/88	2217	5905	17988	16683	27	1931	282.59	1.0045
281		Mar. 24/88	2246	6372	17994	16795	16	2633	282.31	1.0045
282		Mar. 31/88	2177	5573	17969	16933	32	2264	283.08	1.0045
283	D4-55	Mar. 8/88	2466	3352	7197	6392	11	1830	108.67	4.9495
284		Mar. 29/88	2367	3556	7193	6441	7	1803	108.67	4.9495
285		Apr. 14/88	2408	3058	7200	6384	3	1680	109.22	4.9495
286	D4-56	Mar. 8/88	2411	3377	7197	6385	11	1645	108.79	4.9655
287		Mar. 15/88	2529	2990	7202	6425	5	1785	108.82	4.9655
288		Mar. 22/88	2372	2950	7176	6423	20	1885	109.01	4.9655
289	D4-57	Mar. 17/88	2257	3183	7195	6457	11	1921	108.91	4.965
290		Mar. 24/88	2111	3128	7197	6539	6	1895	108.93	4.965
291		Mar. 31/88	2153	3003	7188	6312	13	1986	109.23	4.965
292	D4-58	Mar. 17/88	2284	3283	7195	6495	11	1761	108.84	4.9575
293		Mar. 24/88	2175	3035	7197	6434	6	1911	109.2	4.9575
294		Mar. 31/88	2285	2950	7188	6364	13	1899	109.3	4.9575
295	---	---	---	---	---	---	---	---	---	---
296	Bl-30	Mar. 8/88	1198	4089	17992	17363	26	592	290.46	
297		Mar. 15/88	776	2840	18004	17390	12	755	291.02	

	A	B	C	D	E	F	G	H	I	J
298		Mar. 22/88	834	4053	17939	17294	50	708	289.79	
299	Bl-31	Mar. 17/88	1220	3735	17988	17485	27	540	290.86	
300		Mar. 24/88	864	3778	17994	17430	16	582	291.1	
301		Mar. 31/88	1456	3730	17969	17436	32	560	290.98	
302	Bl-35	Mar. 8/88	324	918	7197	7076	11	168	117.86	
303		Mar. 15/88	234	806	7202	7100	5	185	117.8	
304		Mar. 22/88	206	750	7176	7080	20	143	117.77	
305	Bl-36	Mar. 17/88	447	905	7195	7048	11	25	117.83	
306		Mar. 24/88	346	812	7197	7066	6	210	117.67	
307		Mar. 31/88	253	652	7188	7079	13	114	118.01	
308										
309	E1-50	Feb. 11/88	1955	4633	17995	17185	18	1739	286.38	0.978
310		Feb. 18/88	2151	5333	17996	17083	14	1667	284.7	0.978
311		Feb. 25/88	1857	2036	17999	16982	16	1542	284.63	0.978
312	E1-51	Feb. 11/88	2532	5000	17995	16886	18	1806	285.66	1.0045
313		Feb. 18/88	3042	5198	17996	16962	14	1779	284.73	1.0045
314		Feb. 25/88	2331	5139	17999	16621	16	2278	283.17	1.0045
315	E1-52	Feb. 16/88	2684	5358	18000	16932	5	1862	284.64	1.023
316		Feb. 23/88	2874	5811	17974	16939	24	1768	284.47	1.023
317		Mar. 1/88	2660	5945	18002	16877	16	1650	282.91	1.023
318	E1-53	Feb. 16/88	2503	4940	18000	17004	5	1680	285.78	1.0215
319		Feb. 23/88	3553	5425	17974	16928	24	1614	284.36	1.0215
320		Mar. 1/88	2286	5094	18002	16864	16	1846	284.14	1.0215
321	E1-55	Feb. 11/88	2225	2760	7198	6495	7	1508	110.56	4.9605
322		Feb. 18/88	2176	824	7198	6522	6	1386	110.9	4.9605
323		Feb. 25/88	2495	2685	7200	6575	7	1635	110.62	4.9605
324	E1-56	Feb. 11/88	2285	2428	7198	6514	7	1680	110.9	4.933

	A	B	C	D	E	F	G	H	I	J
325		Feb. 18/88	2201	2783	7198	6551	6	1407	110.98	4.933
326		Feb. 25/88	2198	2715	7200	6556	7	1301	110.94	4.933
327	E1-57	Feb. 16/88	2232	2673	7200	6586	2	1341	111.14	4.943
328		Feb. 23/88	2184	2735	7189	6565	9	1446	110.95	4.943
329		Mar. 1/88	2421	2745	7201	6551	6	1733	110.48	4.943
330	E1-58	Feb. 16/88	2640	2463	7200	6536	2	1537	111.14	4.9575
331		Feb. 23/88	2392	2660	7189	6425	9	1458	110.92	4.9575
332		Mar. 1/88	2508	2783	7201	6473	6	1356	110.31	4.9575
333	E2-50	Feb. 11/88	2467	4108	17995	17304	18	981	288.74	1.027
334		Feb. 18/88	2472	4510	17996	17074	14	1092	288.1	1.027
335		Feb. 25/88	2433	4918	17999	16887	16	1092	286.79	1.027
336	E2-51	Feb. 11/88	2639	4290	17995	17238	18	1017	288.56	1.0205
337		Feb. 18/88	3176	1857	17996	17140	14	1119	287.65	1.0205
338		Feb. 25/88	3484	5093	17999	17052	16	1516	286.35	1.0205
339	E2-52	Feb. 16/88	2763	4338	18000	17246	5	1411	288.18	0.9865
340		Feb. 23/88	2504	4560	17974	17294	24	939	288.24	0.9865
341		Mar. 1/88	2625	4527	18002	17021	16	1045	286.66	0.9865
342	E2-53	Feb. 16/88	2655	3978	18000	17266	5	1278	289.66	0.9975
343		Feb. 23/88	2929	4870	17974	17012	24	1456	287.22	0.9975
344		Mar. 1/88	2987	5682	18002	17208	16	1194	286.13	0.9975
345	E2-55	Feb. 11/88	2899	2063	7198	6786	7	702	114.01	4.961
346		Feb. 18/88	2854	2073	7198	6863	6	988	114.07	4.961
347		Feb. 25/88	2828	2275	7200	6704	7	660	113.6	4.961
348	E2-56	Feb. 11/88	2765	2070	7198	6875	7	683	113.97	4.9645
349		Feb. 18/88	2944	2195	7198	6721	6	872	113.91	4.9645
350		Feb. 25/88	2553	2310	7200	6767	7	725	114.07	4.9645
351	E2-57	Feb. 16/88	2956	2351	7200	6757	2	750	113.81	4.96

	A	B	C	D	E	F	G	H	I	J
352		Feb. 23/88	2989	2296	7189	6717	9	770	113.92	4.96
353		Mar. 1/88	2862	2105	7201	6788	6	866	113.67	4.96
354	E2-58	Feb. 16/88	3029	2205	7200	6900	2	754	114.09	4.9575
355		Feb. 23/88	2694	831	7189	6856	9	528	113.83	4.9575
356		Mar. 1/88	2766	2175	7201	6750	6	816	113.88	4.9575
357	E3-50	Feb. 11/88	2467	1695	17995	17176	18	1222	288	1.0195
358		Feb. 18/88	2114	5008	17996	17070	14	2085	286.43	1.0195
359		Mar. 3/88	2400	6336	18004	16889	13	1862	283.7	1.0195
360	E3-51	Feb. 11/88	2296	4065	17995	17286	18	1235	288.84	1.012
361		Feb. 18/88	2383	4580	17996	17184	14	1541	287.71	1.012
362		Mar. 3/88	2412	2031	18004	16985	13	1474	285.26	1.012
363	E3-52	Feb. 16/88	3508	4398	18000	17164	5	1375	287.86	1.0075
364		Feb. 23/88	3188	4823	17974	17080	24	1320	286.73	1.0075
365		Mar. 1/88	2980	5510	18002	17022	16	1377	285.11	1.0075
366	E3-53	Feb. 16/88	2438	4570	18000	17227	5	1218	287.65	1.011
367		Feb. 23/88	2401	4374	17974	17105	24	1170	286.96	1.011
368		Mar. 1/88	2287	1976	18002	17096	16	1143	286.93	1.011
369	E3-55	Feb. 11/88	2808	2104	7198	6864	7	813	113.68	4.9725
370		Feb. 18/88	2899	2192	7198	6722	6	861	113.38	4.9725
371		Feb. 25/88	2680	3371	7200	6704	7	1001	113.24	4.9725
372	E3-56	Feb. 11/88	2797	2058	7198	6723	7	985	113.76	4.944
373		Feb. 18/88	2975	2197	7198	6736	6	801	113.52	4.944
374		Mar. 3/88	2661	2270	7201	6728	5	874	113.22	4.944
375	E3-57	Feb. 16/88	2848	2228	7200	6752	2	956	113.79	4.966
376		Feb. 23/88	2750	2401	7189	6739	9	780	113.43	4.966
377		Mar. 1/88	2677	893	7201	6708	6	1267	113.1	4.966
378	E3-58	Feb. 16/88	2710	2173	7200	6743	2	773	113.56	4.9495

	A	B	C	D	E	F	G	H	I	J
379		Feb. 23/88	2863	2497	7189	6647	9	1430	113.18	4.9495
380		Mar. 1/88	2708	2258	7201	6764	6	806	113.2	4.9495
381	E4-50	Feb. 11/88	2298	4093	17995	17172	18	1111	287.23	1.0195
382		Feb. 18/88	2503	5110	17996	17036	14	1290	286.46	1.0195
383		Feb. 25/88	2021	4728	17999	17060	16	1209	286.98	1.0195
384	E4-51	Feb. 11/88	2208	4080	17995	17182	18	1176	288.56	1.007
385		Feb. 18/88	2762	5120	17996	17006	14	1350	286.28	1.007
386		Mar. 3/88	2032	5505	18004	16853	13	1589	284.83	1.007
387	E4-52	Feb. 16/88	2696	4420	18000	17104	5	1260	287.65	1.003
388		Feb. 23/88	2730	4635	17974	17168	24	1149	286.96	1.003
389		Mar. 1/88	2805	5088	18002	16986	16	1352	285.51	1.003
390	E4-53	Feb. 16/88	3704	5346	18000	16981	5	1305	286.39	1.021
391		Feb. 23/88	2588	1947	17974	17051	24	1526	286.53	1.021
392		Mar. 1/88	2138	5312	18002	17045	16	1284	286.05	1.021
393	E4-55	Feb. 11/88	2198	2165	7198	6731	7	787	113.34	4.924
394		Feb. 18/88	2371	3056	7198	6743	6	900	113.22	4.924
395		Feb. 25/88	2085	2278	7200	6649	7	924	113.15	4.924
396	E4-56	Feb. 11/88	2409	2198	7198	6669	7	1544	113.45	4.963
397		Feb. 18/88	2431	2115	7198	6762	6	1160	113.18	4.963
398		Feb. 25/88	2611	2390	7200	6728	7	917	112.96	4.963
399	E4-57	Feb. 16/88	2413	2393	7200	6689	2	855	113.29	4.933
400		Feb. 23/88	2273	2362	7189	6719	9	879	113.2	4.933
401		Mar. 1/88	2449	878	7201	6671	6	1043	112.81	4.933
402	E4-58	Feb. 16/88	2592	2550	7200	6675	2	1092	113.27	4.976
403		Feb. 23/88	2450	934	7189	6667	9	861	112.85	4.976
404		Mar. 1/88	2829	2380	7201	6591	6	1203	112.57	4.976
405										

	A	B	C	D	E	F	G	H	I	J
406	Bl-52	Feb. 11/88	1188	3328	17995	17514	18	501	292.71	
407		Feb. 18/88	1610	3235	17996	17567	14	585	292.15	
408		Feb. 25/88	1164	3680	17999	17453	16	468	290.87	
409	Bl-53	Feb. 16/88	1995	2815	18000	17627	5	572	293.11	
410		Feb. 23/88	1547	3513	17974	17478	24	596	291.44	
411		Mar. 1/88	1108	3267	18002	17500	16	563	291.21	
412	Bl-57	Feb. 11/88	359	748	7198	7091	7	120	118.33	
413		Feb. 18/88	454	756	7198	7042	6	29	118.03	
414		Feb. 25/88	333	833	7200	7103	7	132	117.79	
415	Bl-58	Feb. 16/88	344	675	7200	7156	2	138	118.42	
416		Feb. 23/88	512	843	7189	7095	9	132	118.04	
417		Mar. 1/88	402	930	7201	7059	6	135	117.88	

A2.2 Raw Data For CINAA Experiments Performed on Glass Panes

Contained in this section are results for the CINAA experiments described in section 3.2.5. Hafnium analyses were performed on AFG- and Pittsburgh-produced glass panes. The results for the AFG samples appear in rows 3 to 39 while the Pittsburgh results are shown in rows 41 to 97. Appearing in column A are subsample labels. Glass panes are indicated by numbers to the left of the hyphen, numbers to the right designate subsamples. A description of the values contained in each of the remaining columns appears in section A2.1 of this appendix. All of the above values were taken directly from output produced by a spectral peak searching routine supplied by Aptec Engineering Limited. At the end of each data set are blank values. Separation of the blanks from the subsamples of a particular flat glass manufacturer is accomplished by using a dashed line. A blank line separates the glasses produced by each manufacturer.

	A	B	C	D	E	F	G	H	I	J
1	Sub-	Date	Raw Counts	Bkgrd. Counts	Plsr.	Plsr.	Bkgrd.	Bkgrd.	Live Time	Mass
2	sample		Hf	Hf	Cnts. 1	Cnts. 2	Cnts. 1	Cnts. 2	(seconds)	(mg)
3	4-50	4-May-89	2444	7522	17842	14625	10	3323	284.66	1.0065
4	4-51	11-May-89	2033	6802	17817	15009	16	3519	285.42	1.0185
5	4-52	4-May-89	2713	6799	17842	15140	10	4433	284.25	1.02
6	4-53	11-May-89	1628	8304	17817	15658	16	5505	284.79	1.0565
7	6-50	4-May-89	2944	10538	17842	14975	10	3350	284.74	0.9905
8	6-51	4-May-89	1571	6883	17842	15122	10	2889	284.2	1.01
9	6-52	11-May-89	1448	6123	17817	15098	16	4163	285.51	1.018
10	6-53	11-May-89	2003	5379	17817	15235	16	3675	284.94	0.9865
11	13-50	4-May-89	2074	6874	17842	15229	10	4316	284.46	1.045
12	13-51	11-May-89	1375	6110	17817	15913	16	3687	285.78	1.0125
13	13-52	4-May-89	2250	8604	17842	15300	10	4462	283.87	1.0395
14	13-53	11-May-89	1610	6272	17817	15074	16	3771	284.33	1.0225
15	15-50	18-May-89	1690	7336	17528	14546	148	4236	284.29	1.012
16	15-51	11-May-89	1838	7640	17817	15129	16	3933	285.11	0.9815
17	15-52	4-May-89	1699	5760	17842	15025	10	2889	285.26	1.0185
18	15-53	4-May-89	1694	6636	17842	15418	10	3450	285.37	1.0245
19	4-55	4-May-89	1465	3523	7137	5193	4	2533	110.99	4.967
20	4-56	11-May-89	1343	3731	7127	5606	6	3427	111.3	4.96
21	4-57	4-May-89	1326	3705	7137	5313	4	2280	111.01	4.9695
22	4-58	11-May-89	1313	3594	7127	5086	6	2624	111.11	4.9745
23	6-55	4-May-89	1541	3472	7137	5650	4	2892	112.24	4.9855
24	6-56	4-May-89	1405	4368	7137	5205	4	3171	110.93	4.968
25	6-57	11-May-89	1366	3528	7127	5557	6	3278	111.34	4.974
26	6-58	11-May-89	1026	3718	7127	5432	6	2774	111.53	4.979
27	13-55	4-May-89	2079	6300	7137	5652	4	3510	111.02	4.964

	A	B	C	D	E	F	G	H	I	J
28	13-56	11-May-89	1420	2910	7127	5278	6	3170	111.32	4.958
29	13-57	4-May-89	1618	4292	7137	4884	4	2190	111.07	4.9535
30	13-58	11-May-89	1578	3577	7127	5668	6	3408	111.14	4.954
31	15-55	11-May-89	1294	3575	7127	5494	6	3000	111.24	4.9685
32	15-56	11-May-89	1672	4105	7127	5491	6	3600	111.33	4.9755
33	15-57	4-May-89	1851	4769	7137	5340	4	3045	111.01	4.9775
34	15-58	4-May-89	1617	4653	7137	4935	4	2240	111.08	4.956
35	---	---	---	---	---	---	---	---	---	---
36	Bla-7	11-May-89	1354	3546	17817	16621	16	836	291.14	
37	Bla-5	4-May-89	1117	4042	17842	16884	10	736	291.77	
38	Bla-8	18-May-89	824	1124	7011	6663	59	255	117.34	
39	Bla-6	4-May-89	654	1169	7137	6701	4	280	117.06	
40										
41	1-50	Jan. 12/89	2023	5087	17580	15183	126	3415	286.8	0.9945
42	1-51	Jan. 17/89	1951	6571	17454	15563	168	5208	285.96	1.012
43	1-52	Jan. 19/89	2438	4691	17479	14736	202	2465	286.6	1.015
44	1-53	Jan. 10/89	2108	5406	17892	15331	29	2552	286.56	1.018
45	8-50	Jan. 12/89	2276	6058	17580	14970	126	3012	286.44	0.997
46	8-51	Jan. 10/89	2552	6272	17892	14802	29	2240	286.9	0.981
47	8-52	Jan. 17/89	2372	7569	17454	15705	168	4567	287.29	0.9995
48	8-53	Jan. 19/89	2275	6454	17479	15464	202	2592	286.86	1.03
49	13-50	Jan. 12/89	2518	7862	17580	15563	126	3350	286.24	0.994
50	13-51	Jan. 19/89	2164	7110	17479	15037	202	2065	286.14	1.0265
51	13-52	Jan. 17/89	3391	5736	17454	15431	168	4140	286.27	1.0125
52	13-53	Jan. 10/89	2125	5028	17892	15392	29	2794	287.73	1.0065
53	37-50	Jan. 10/89	2234	5508	17892	15290	29	2940	286.91	0.9925
54	37-51	Jan. 19/89	2373	8270	17479	14812	202	3289	285.14	1.019

	A	B	C	D	E	F	G	H	I	J
55	37-52	Feb. 7/89	1432	6951	17644	15140	68	4205	285.08	1.0055
56	37-53	Jan. 12/89	2915	5902	17580	15180	126	3588	285.82	1.026
57	41-50	Jan. 12/89	2626	5964	17580	14521	126	3733	285.11	1.0095
58	41-51	Jan. 17/89	2723	8253	17454	15199	168	3864	286.23	0.991
59	41-52	Jan. 19/89	2554	8469	17479	15294	202	2388	286.48	1.0105
60	41-53	Jan. 10/89	2289	6615	17892	14954	29	3157	286.02	1.0235
61	48-50	Jan. 19/89	2305	8739	17479	15133	202	2415	286.35	0.9835
62	48-51	Jan. 10/89	1810	4690	17892	15583	29	3233	287.32	1.005
63	48-52	Jan. 12/89	2070	5225	17580	15031	126	3408	285.8	1.0085
64	48-53	Feb. 7/89	1811	5094	17644	14984	68	2366	287.01	0.989
65	1-55	Jan. 12/89	1888	2466	7032	5573	50	1576	113.5	4.9795
66	1-56	Jan. 17/89	1851	3440	6982	5813	67	2585	113.24	4.9335
67	1-57	Jan. 19/89	1953	2872	6992	5992	81	1529	113.75	4.951
68	1-58	Jan. 10/89	1830	2936	7157	5888	12	1482	113.99	4.959
69	8-55	Jan. 12/89	1686	2887	7032	5802	50	1377	114.06	4.9235
70	8-56	Feb. 7/89	1984	3157	7058	5558	27	1351	113.45	4.951
71	8-57	Jan. 17/89	2040	3424	6982	6033	67	2772	113.3	4.961
72	8-58	Jan. 19/89	2181	3456	6992	5952	81	1390	113.67	4.9795
73	13-55	Jan. 12/89	1678	2496	7032	5852	50	1662	113.59	4.979
74	13-56	Jan. 19/89	1970	3789	6992	5433	81	1189	113.64	4.948
75	13-57	Jan. 17/89	2236	3048	6982	5851	67	2702	113.64	4.979
76	13-58	Jan. 10/89	1933	3192	7157	5300	12	1617	113.71	4.9575
77	37-55	Jan. 10/89	2186	2322	7157	5838	12	1978	113.45	4.9725
78	37-56	Jan. 19/89	2396	4762	6992	5980	81	1483	113.6	4.967
79	37-57	Jan. 17/89	1923	2807	6982	5648	67	2133	113.65	4.9645
80	37-58	Jan. 12/89	1980	3136	7032	5658	50	1485	113.47	4.965
81	41-55	Jan. 12/89	2510	3045	7032	5802	50	1710	113.48	4.9575

	A	B	C	D	E	F	G	H	I	J
82	41-56	Jan. 17/89	2538	3145	6982	6027	67	2321	113.72	4.9725
83	41-57	Jan. 19/89	1997	3900	6992	5791	81	1533	113.8	4.9725
84	41-58	Jan. 10/89	1924	3465	7157	5820	12	1512	113.77	4.9815
85	48-55	Jan. 19/89	2055	3366	6992	5856	81	1396	113.58	4.9625
86	48-56	Jan. 10/89	1645	2795	7157	5272	12	1469	113.75	4.955
87	48-57	Jan. 12/89	2356	3717	7032	5772	50	1921	113.61	4.9585
88	48-58	Jan. 17/89	2970	3052	6982	5479	67	2336	113.4	4.9775
89	---	---	---	---	---	---	---	---	---	---
90	Bl-1	Jan. 10/89	1391	3833	17892	16490	29	1184	290.49	
91	Bl-1	Feb. 7/89	1110	3350	17644	16067	68	1010	291.54	
92	Bl-4	Jan. 19/89	1047	3270	17479	16201	202	900	290.56	
93	Bl-4	Feb. 7/89	2311	5778	17644	16143	68	1218	290.72	
94	Bl-3	Jan. 10/89	730	825	7157	6786	12	261	117.64	
95	Bl-3	Feb. 7/89	387	786	7058	6594	27	333	117.57	
96	Bl-2	Jan. 12/89	709	972	7032	6706	50	255	117.58	
97	Bl-2	Jan. 19/89	525	648	6992	6838	81	231	117.45	

A2.3 Short-Lived Thermal Neutron Reactions ($t_{1/2}$ < 65 Seconds)

Appearing in this section is a table of thermal neutron reactions that may be studied by CINAA. Also appearing in the table are half-lives for the short-lived radionuclides of interest, cross sections for the thermal neutron capture reactions, target abundances and finally the energies and intensities of the most intense γ-ray for each reaction. Unreported intensities signify the presence of only one γ-ray energy. This information was obtained from several sources[134-136].

Table A4.1.1 Short-Lived Thermal Neutron Reactions ($t_{1/2}$ < 65 Seconds).

Reaction	$t_{1/2}$, s	σ, barns	Target Abundance, %	E keV	Intensity, %
$^{72}Ge(n, \gamma)^{73m}Ge$	0.53	1	27.37	54	9
$^{37}Cl(n, \gamma)^{38m}Cl$	0.74	0.005	24.47	660	100
$^{206}Pb(n, \gamma)^{207m}Pb$	0.80	0.03	21.7	570	98
$^{166}Er(n, \gamma)^{167m}Er$	2.3	12	33.41	208	43
$^{115}In(n, \gamma)^{116m}In$	2.16	4	95.77	164	
$^{177}Hf(n, \gamma)^{178m}Hf$	4.3	1.4	18.56	427	97
$^{182}W(n, \gamma)^{183m}W$	5.3	0.5	26.4	108	19
$^{176}Yb(n, \gamma)^{177m}Yb$	6.5	7	12.73	104	65
$^{19}F(n, \gamma)^{20}F$	11.56	0.01	100	1633	100
$^{80}Kr(n, \gamma)^{81m}Kr$	13	15	2.27	190	65
$^{115}In(n, \gamma)^{116}In$	13.4	45	95.77	1293	1
$^{198}Pt(n, \gamma)^{199m}Pt$	14.1	0.03	7.19	393	90
$^{76}Se(n, \gamma)^{77m}Se$	17.5	22	9.02	161	50
$^{178}Hf(n, \gamma)^{179m}Hf$	18.6	50	27.1	217	94
$^{45}Sc(n, \gamma)^{46m}Sc$	19.5	10	100	142	

$^{106}Pd(n, \gamma)^{107m}Pd$	21.3	0.29	27.3	214	100
$^{109}Ag(n, \gamma)^{110}Ag$	24.4	89	48.65	658	4
$^{18}O(n, \gamma)^{19}O$	29	0.00021	0.20	197	97
$^{164}Dy(n, \gamma)^{165m}Dy$	32	2000	28.18	complex spectrum	
$^{22}Ne(n, \gamma)^{23}Ne$	37.6	0.04	8.82	439	33
$^{103}Rh(n, \gamma)^{104}Rh$	43	144	100	556	2
$^{168}Yb(n, \gamma)^{169m}Yb$	46	11000	0.14	24	100
$^{74}Ge(n, \gamma)^{75m}Ge$	48	0.2	36.74	139	34
$^{76}Ge(n, \gamma)^{77m}Ge$	54	0.1	7.67	215	21
$^{138}Ce(n, \gamma)^{139m}Ce$	55	7	0.26	754	100
$^{85}Rb(n, \gamma)^{86m}Rb$	62.4	0.1	72.15	556	100

Appendix 3

A3.1 Raw Data For EINAA Experiments Performed on Nineteen Glass Samples

The results for the epithermal instrumental neutron activation analysis (EINAA) experiments described in chapter 4 are contained in this appendix. Nineteen glass fragments provided by an RCMP forensic laboratory were analysed for sodium and aluminum. Subsample labels appear in column A. The letters and numbers appearing to the left of the hyphen indicate a glass sample, the numbers on the right designate a subsample. The analysis date for each subsample is listed in column B. Contained in columns C to E are the raw counts obtained for Na-1 (1369-keV photopeak of sodium), Na-2 (2754-keV photopeak of sodium) and Al while columns F to H represent the background counts underlying the photopeaks. In column I, average counts for a pulser (pulser 1) in the absence of a glass subsample are listed. Determination of this value required averaging the pulser counts obtained prior to and immediately following a day's experiments. Pulser 2 (column J) represents the counts resulting when the same pulser was counted during the acquisition of a glass subsample spectrum. Columns K and L are the background counts associated with the two pulser peaks. Appearing in column M are clock times; the live time was 600 seconds for all subsamples. The above values were taken directly from output produced by a spectral peak searching routine (PREP 10) supplied by Nuclear Data. Finally, in column N are the subsample masses in milligrams. The uncertainty associated with every measurement is ± 0.0017 milligrams. Blank values appear at the end of

the data set and are separated from the subsamples by a dashed line. A blank line separates glasses with different refractive index values.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Sub-	Date	Raw	Counts		Bkgr	d. Co	unts	Plsr.	Plsr.	Bkgrd.	Bkgrd.	ClockTime	Mass
2	sample		Na-1	Na-2	Al	Na-1	Na-2	Al	Cnts. 1	Cnts. 2	Cnts. 1	Cnts. 2	(seconds)	(mg)
3	A1-2s	Dec. 15/86	231	91	2042	325	17	38	43812	43777	2	0	603.5	0.3632
4	A2-1	Dec. 15/86	227	125	1767	166	5	59	43812	43776	2	3	603.5	0.3269
5	A3-1	Jan. 12/87	54	24	541	60	0	26	43794	43762	2	3	603.1	0.1202
6	A3-1s	Dec. 8/86	79	29	613	35	0	9	43759	43747	0	0	603.1	0.137
7	A3-4	Dec. 8/86	213	103	1976	253	0	30	43759	43732	0	10	603.5	0.4562
8	A5-1	Dec. 8/86	194	104	1806	96	0	30	43759	43720	0	6	603.4	0.4272
9														
10	B1-2'	Dec. 8/86	258	104	2173	170	0	64	43759	43715	0	3	603.5	0.4515
11	B2-1s	Dec. 15/86	225	109	1878	69	7	55	43812	43768	2	0	603.5	0.3698
12	B3-1	Dec. 15/86	97	48	963	49	0	60	43812	43806	2	0	603.2	0.1872
13	B3-2	Dec. 8/86	65	14	398	7	0	0	43759	43736	0	0	603	0.0922
14	B4-1'	Jan. 12/87	105	48	639	33	0	12	43794	43769	2	3	603.1	0.1336
15	B4-2s'	Jan. 12/87	152	76	1252	66	0	9	43794	43781	2	0	603.3	0.2878
16														
17	C1-1	Dec. 8/86	193	98	2051	111	0	38	43759	43724	0	3	603.5	0.4277
18	C1-1s	Dec. 8/86	53	12	422	19	0	0	43759	43763	0	0	603	0.079
19	C2-1s	Jan. 12/87	96	30	583	76	0	14	43794	43785	2	3	603.1	0.1193
20	C2-2'	Dec. 8/86	205	110	2066	120	0	25	43759	43726	0	3	603.5	0.4691
21	C3-1s	Dec. 15/86	345	155	2515	114	0	50	43812	43779	2	7	603.6	0.4757
22	C3-2s	Jan. 12/87	262	122	2388	172	0	53	43794	43765	2	0	603.6	0.4613
23														
24	D1-1	Jan. 12/87	160	70	1290	71	0	32	43794	43809	2	0	603.3	0.252
25	D1-2	Jan. 12/87	74	26	606	69	0	25	43794	43752	2	0	603.1	0.1234
26	D2-1s	Dec. 15/86	247	80	1706	120	0	37	43812	43804	2	0	603.4	0.3379
27	D3-1s	Dec. 15/86	147	89	1492	215	0	30	43812	43783	2	0	603.3	0.2886

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
28	D4-2s	Dec. 15/86	250	121	2165	149	8	69	43812	43791	2	4	603.6	0.4193
29														
30	E1-1	Jan. 12/87	96	46	556	37	0	4	43794	43763	2	0	603.1	0.1211
31	E1-2s	Dec. 8/86	115	61	755	149	0	18	43759	43722	0	0	603.1	0.1774
32	E2-1	Dec. 15/86	69	37	660	35	4	18	43812	43796	2	0	603.1	0.1373
33	E2-1s'	Dec. 8/86	224	115	2066	191	0	58	43759	43727	0	0	603.5	0.5049
34	E3-1s	Dec. 15/86	203	90	1251	87	0	40	43812	43788	2	3	603.3	0.2625
35	E4-1	Dec. 15/86	200	98	1471	128	4	52	43812	43781	2	3	603.4	0.3052
36	---	---	---	---	---	---	---	---	---	---	---	---	---	---
37	BL-2	Dec. 8/86	4	0	4	0	0	0	43759	43741	0	0	602.9	
38	BL-1'	Dec. 15/86	11	9	15	6	0	0	43812	43801	2	0	602.9	
39	BL-5s	Jan. 12/87	15	0	16	0	0	4	43794	43776	2	0	602.9	